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ADVANCES IN CHEMICAL PHYSICS

VOLUME V

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ADVANCES IN CHEMICAL PHYSICS

Edited by **I. PRIGOGINE**
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VOLUME V

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INTRODUCTION

In the last decades, chemical physics has attracted an ever increasing amount of interest. The variety of problems, such as those of chemical kinetics, molecular physics, molecular spectroscopy, transport processes, thermodynamics, the study of the state of matter, and the variety of experimental methods used, makes the great development of this field understandable. But the consequence of this breadth of subject matter has been the scattering of the relevant literature in a great number of publications.

Despite this variety and the implicit difficulty of exactly defining the topic of chemical physics, there are a certain number of basic problems that concern the properties of individual molecules and atoms as well as the behavior of statistical ensembles of molecules and atoms. This new series is devoted to this group of problems which are characteristic of modern chemical physics.

As a consequence of the enormous growth in the amount of information to be transmitted, the original papers, as published in the leading scientific journals, have of necessity been made as short as is compatible with a minimum of scientific clarity. They have, therefore, become increasingly difficult to follow for anyone who is not an expert in this specific field. In order to alleviate this situation, numerous publications have recently appeared which are devoted to review articles and which contain a more or less critical survey of the literature in a specific field.

An alternative way to improve the situation, however, is to ask an expert to write a comprehensive article in which he explains his view on a subject freely and without limitation of space. The emphasis in this case would be on the personal ideas of the author. This is the approach that has been attempted in this new series. We hope that as a consequence of this approach, the series may become especially stimulating for new research.

Finally, we hope that the style of this series will develop into something more personal and less academic than what has become

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the standard scientific style. Such a hope, however, is not likely to be completely realized until a certain degree of maturity has been attained—a process which normally requires a few years.

At present, we intend to publish one volume a year, but this schedule may be revised in the future.

In order to proceed to a more effective coverage of the different aspects of chemical physics, it has seemed appropriate to form an editorial board. I want to express to them my thanks for their cooperation.

I. PRIGOGINE

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NEW DEVELOPMENTS IN THE ONE-ELECTRON THEORY OF π-ELECTRON SYSTEMS

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I. INTRODUCTION

From the physicist's point of view, a one-electron treatment of molecular electron systems is a first approximation. The explicit inclusion of interelectronic forces means an improvement of the theory and leads to a closer approximation. From the chemist's point of view the situation is rather different. Certainly the chemist is interested in the properties of specific molecules, but his main interest lies in the detection of properties of whole groups of substances. He wants to know the variation of properties within such a group, and he has the feeling that this type of question is reasonable. Now the Schrödinger equations of two different molecules are quite different and there is no regular similarity between them.

The physicist aspires to find the correct solutions of both equations. When he has done his task perfectly, he will have two rows of figures, one for each molecule. He has all the data about each molecule, but in this way he can never get an insight into the relations between the properties of the molecules of a whole group of substances. There seems to be only one way of getting a physical answer to the typical question of the chemist, which we have described above. One should find a model which to a certain degree is artificial and is a simplified picture of the molecules of a group of substances. The model should be as close as possible to the real molecules to be described, and, on the other hand, it should be possible to adjust the model to the different molecules of a group of substances by properly adjusting one or more parameters of the model.

Looked at from the physicist's point of view the treatment of such models is, as we have said, a first approximation. From the chemist's point of view, the treatment of simplified models, which are suited to represent the molecules of a whole group of substances, is the main task which can be done by physical means. The improvements desired by the physicist to secure a theory which is better for his purposes are not necessarily improvements from the chemist's point of view. It might be useful to explain this further by a well-known example.

Chemists know that valence theory and its graphical symbol describing a chemical bond between two atoms have proved extremely useful for ordering a very great number of chemical facts. Now the work of Heitler and London has shown that there is a close analogy to the chemist's bond line in an approximate quantum-theoretical concept of the covalent bond. This result of Heitler and London has become the basis of the well-known theory of the valence bond.

On the other hand, quantum chemists know well that this analogy disappears as the quantum-theoretical treatment of molecular electron systems is improved. The analogy of quantum chemical results and their numerical exactness is, in a certain way, complementary.

The physicist likes simplified models because their mathematical treatment is much easier. The chemist is not unhappy that this is so, but, as we have shown, his love for simplified models in a first line does not have this origin.

During the last fifteen years we have seen the outcome of many so-called improvements in quantum chemistry. Because of the above-mentioned circumstances we have the impression that one should again concentrate the quantum chemist's interest on the theory of simplified models and therefore on one-electron theories. We want to describe the results of a group of investigations on the one-electron theory of π-electron systems, which were done by the author and his coworkers. We think that the results of these investigations can not only prove the importance of one-electron theories but also show that it is sometimes better to investigate simple theories very carefully than to start formal improvements too early.

One-electron theories are characterized by the supposition that all electrons of the molecule move in the same field. This field is called the effective field and it resembles the interaction between the electron and the system of the core of the atoms on the one side and the interaction between the electrons themselves on the other side. A certain one-electron theory is characterized by the problem of zeroth approximation, which has been used as the starting point. The problem of zeroth approximation determines the type of the eigenfunctions. One-electron theories of π-electron systems have been developed in two ways. These are in systematic order:

1. In analogy to the model used by Sommerfeld in the theory of electron states of crystals Schmidt, Kuhn, and others have developed the so-called free-electron theories.
2. In the theory of electron states of crystals Bloch has started his investigations from a point of view which in a certain sense is opposite to the point of view of Sommerfeld. He tried to describe the electronic states of a crystal as a linear combination of atomic eigenfunctions. His method was transferred to the theory of π-electron systems by Hückel, who became the founder of this field of research. The Hückel theory has a wider field of application, while the free-electron theories can only be used for the analysis of spectroscopic data.

The Hückel theory, at least in principle, can be applied to the analysis of spectroscopic data and in the interpretation of caloric energy values such as resonance energies. It is well-known that the application of the free-electron theories in the spectroscopic field gives much better results than the application of the Hückel theory in the same field, if the values of the semiempirical parameters of the Hückel theory are taken from the analysis of resonance energies. The Hückel theory seems to be very inconsistent in so far as the relation between the values of the resonance integral β, which are determined from the analysis of resonance energies on one side and the analysis of spectroscopic data on the other side, amounts to the value of three.

Until recently quantum chemists have had the opinion that this discrepancy had its real root in the poor approximation of the one-electron scheme. Now during the last years Scheibe detected a spectroscopic regularity of great importance which could not be explained either by free-electron theories or by the Hückel theory. Scheibe has stated that the energetic distance between the ionization limit and the first excited electron state, which has the same multiplicity as the ground state, in all molecules with π-electron systems has nearly the same value, although the energetic distance between the ground state and the first-excited state in the different molecules is very different.

One cannot expect that this fact can be explained by free-electron theories, because it uses infinitely high potential walls around the molecule and so is not apt to describe ionization phenomena. On the other hand, the Hückel theory had so far proved to be unable to explain normal spectroscopic facts. Now the phenomenon detected by Scheibe seems to be of such a fundamental nature that it was rather unreasonable that it should be impossible to explain such a fundamental phenomenon in the simple one-electron scheme. Therefore, we started a careful re-examination of Hückel's theory.

II. THE ONE-ELECTRON STATES OF THE ETHYLENE MOLECULE

Hückel's theory gives two molecular electronic states for the electron system of the ethylene molecule, a bonding one and an antibonding one. Both states in first approximation are described by linear combinations of the atomic $2p$ eigenfunctions of the two carbon atoms. We call the energies of the two states $E(b)$ and

$E(l)$. If the energy of the atomic $2p$ term is $E(2p)$ the Hückel theory gives the relations

$$E_b - E_{2p} = \alpha + \beta \tag{1}$$

$$E_l - E_{2p} = \alpha - \beta \tag{2}$$

$$\alpha > 0, \qquad \beta < 0, \qquad |\beta| \gg \alpha \tag{3}$$

α is the Coulomb integral and β the characteristic resonance integral of Hückel's theory. According to (1), (2), and (3) the two-molecular terms should be nearly symmetrical to the atomic $2p$ term.

It is well known that the ground state of the molecule belongs to the electron configuration b^2. The ground state of the molecule is a singlet. To the configuration b^1l^1 belong the second singlet $2(^1)$ and a triplet $1(^3)$. The two configurations and the lower part of the term system of the molecule are given in Fig. 1.

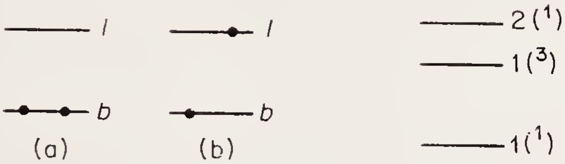


Fig. 1

It is well known that the splitting of the configuration b^1l^1, which leads to the two terms of the molecule $2(^1)$ and $1(^3)$ of the molecule, cannot be described in a one-electron scheme. Only a next step of approximation which regards the true repulsion between the electrons can give the energy difference between $2(^1)$ and $1(^3)$. The difference between the energies $E_{b^1l^1}$ and E_{b^2}, which in the one-electron scheme corresponds to both configurations b^1l^1 and b^2 and which is identical with the distance of the one-electron states l and b can be identified neither with the empirical difference $E_{2(^1)} - E_{1(^1)}$ nor with the difference $E_{1(^3)} - E_{1(^1)}$.

It is known from the treatment of analogous two-electron problems that the inclusion of electron repulsion gives the result

$$E_{2(^1)} - E_{b^1l^1} = C + A \tag{4}$$

$$E_{1(^3)} - E_{b^1l^1} = C - A \tag{5}$$

C is a Coulomb integral and A an exchange integral. Figure 2 gives the genetical relations between the terms. From (1) and (2) follows

$$E_{b^1l^1} = \tfrac{1}{2}(E_{2(^1)} + E_{1(^3)}) - C \tag{6}$$

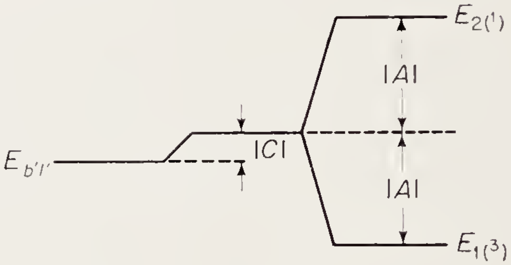


Fig. 2

If we call the Coulomb integral between two b electrons C', we get the second equation

$$E_{1(^1)} - E_{b^2} = C' \tag{7}$$

From (6) and (7) follows

$$\begin{aligned} E_l - E_b &= E_{b^1l^1} - E_{b^2} \\ &= \tfrac{1}{2}(E_{2(^1)} + E_{1(^3)}) - E_{1(^1)} - (C - C') \end{aligned} \tag{8}$$

It is reasonable to assume that the difference between the two Coulomb integrals is small compared with the exchange integral A. In this approximation we have

$$E_l - E_b = \tfrac{1}{2}(E_{2(^1)} + E_{1(^3)}) - E_{1(^1)} \tag{9}$$

The following empirical values are known[7]:

$$E_{2(^1)} - E_{1(^1)} = 7.6 \text{ ev} \tag{10}$$

$$E_{1(^3)} - E_{1(^1)} = 6.9 \text{ ev} \tag{11}$$

So according to (9) we get

$$E_l - E_b = 7.25 \text{ ev} \tag{12}$$

In the following we shall use the value

$$E_l - E_b = 6.6 \text{ ev}$$

In this way to a certain degree, the neglect of the difference of the two Coulomb integrals can be compensated. The ionization energy of the ethylene molecule is 10.4 ev. So the one-electron state b is 10.4 ev below the ionization limit. The relative position of the one-electron states and the ionization limit is shown in Fig. 3.

A formal half of the ethylene molecule, which we may call the "constituent group", can be formed in the following way. We add to a carbon atom in the ground state $C2s^22p^2\ {}^3P$ the energy of ~ 7 ev and bring it to the trigonal valence state $Csp_{tr}{}^3$. Then the σ-bonds are formed, and we get the σ-bond energy B. The corresponding positive ion of the constituent group can be formed in an analogous way. Adding 11.2 ev to a carbon atom, we get the positive carbon ion in its ground state $C^+2s^22p^2p$. Then again ~ 7 ev are necessary for the excitation to the trigonal valence state $C^+sp_{tr}{}^2$ of the positive carbon ion. Finally, the σ-bonds are formed, and, in a first approximation, we should get the same σ-bond energy B. Thus far, the value of the ionization energy of the constituent group should be nearly the same as the value of the ionization energy of the carbon atom (11.2 ev); but we have overlooked two things. When the carbon ion in the trigonal valence state is combined with its ligands to form σ-bonds, the interaction between the charge situated on the carbon ion and the formally neutral ligand atoms contributes a positive amount of energy of the order of magnitude of 1 ev, which hitherto has been

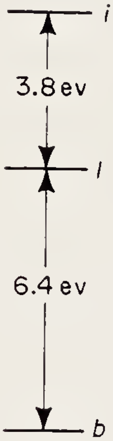


Fig. 3

disregarded. This effect should increase the ionization energy of the constituent group. But, according to approximate calculations of Hellmann, which can be applied here, the induction of electric moments in the formally neutral ligand atoms produced by the charge of the carbon ion should lower the ionization energy by several ev's. So the ionization energy of the constituent group should be much lower than 11.2 ev. These statements do not concern the free methyl radical, because this molecule in its ground state is not necessarily flat, and its ionization energy cannot be compared directly with the ionization energy of the formal half of an ethylene molecule.

The ionization energy of the constituent group must certainly be lower than the ionization energies of all aromatic hydrocarbons. That follows from the fact that ionization of an aromatic hydrocarbon molecule means the removal of an electron from a bonding molecular electronic state. From known values for the ionization energies of aromatic hydrocarbons, one can see that these values converge with increasing number, n, of carbon atoms in the molecule to 5.4 ev. We take this value as the ionization energy of the constituent group. So the "atomic $2p$-state", which is the starting point of Hückel's theory, lies 5.4 ev below the ionization limit. Between this state and the ionization limit there lie all the higher atomic states from $3p$ on. The Rydberg correction for the $3p$ state is certain to be small, so that its distance from the onization limit should be approximately 1.5 ev.

III. THE BASIC IDEA

Figure 4 shows that the bonding and the antibonding molecular electronic states are far from lying symmetrically to the atomic $2p$ state. It seems to be quite unreasonable that the one-electron scheme is such a poor approximation. One should look for a natural explanation of the discrepancy. Figure 4 shows in which direction this explanation is to be sought. The energetical distance between the two terms b and l is greater than the distance of the $2p$ term from the ionization limit.

Under such circumstances it is impossible to expect that a theory which uses only atomic $2p$ states can explain all essential phenomena qualitatively. The necessary extension seems to be quite straightforward. Besides atomic $2p$ states, one should add higher atomic states to the basis to get the molecular eigenfunctions in a good approximation. Because of combination–selection rules only such functions can be used which have the same symmetry character as Hückel's $2p$ functions. It is difficult to follow this program fully. Because of the reasons given above it seems to be impossible to limit the number of higher atomic states. Practically, there is only the possibility of using atomic $3p$ eigenfunctions besides the $2p$ eigenfunctions. So, in a certain sense, the $3p$ eigenfunctions become the representatives of all higher functions. Though this practical difficulty exists at first, we shall develop the theory in a general way.

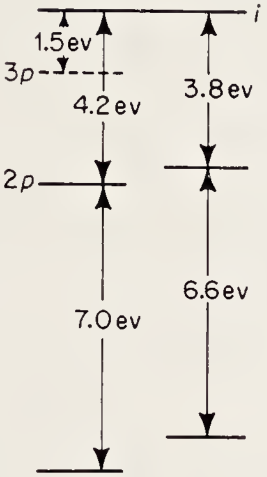


Fig. 4

IV. THE STRUCTURE MATRIX

With regard to the development of the theory it is very useful to define a matrix which we have called the structure matrix. The diagonal elements of the structure matrix (an analogous matrix has been defined by Ham and Rüedenberg as a "topological matrix") are zero

$$s_{jj} = 0 \tag{13}$$

The off-diagonal elements of the structure matrix are 1 or 0. They are 1 if the indices of the element are the numbers of neighboring atoms in the molecule. Otherwise the off-diagonal elements are zero

$$s_{jj'} = \begin{matrix} 1 \\ 0 \end{matrix} \tag{14}$$

The structure matrix has eigenvectors. The jth component of the normalized eigenvector belonging to the ith eigenvalue of the structure matrix ρ_i we call c_{ij}. The eigenvectors are to be determined from the equations

$$\sum_{j}\sum_{j'} c^{\star}_{ij} c_{i'j'} s_{jj'} = 0 \qquad \text{for} \qquad \dot{z}' \neq \dot{z} \tag{15}$$

The relation between the eigenvectors and the eigenvalues of the structure matrix are given by

$$\sum_{j}\sum_{j'} c^{\star}_{ij} c_{ij'} s_{jj'} = \rho_i \tag{16}$$

In the following it is to be kept in mind that the eigenvectors and the eigenvalues of the structure matrix are determined by the structure of the molecule. Especially the eigenvalues are characteristic numbers of the molecule. We call them the Hückel numbers. It is important to see that they are really independent of energetic considerations.

V. FORMAL DEVELOPMENT OF THE THEORY

$\psi_j^{(k)}$ may be an atomic eigenfunction of the same symmetry type as Hückel's $2p$ functions. k is the principal quantum number and j is the number of the atom. In the following we shall use the functions

$$\psi_j^{(k)} \qquad k = 2, 3, \ldots, m \qquad j = 1, 2, \ldots, n \tag{17}$$

We allow that m may go to infinity. The $\psi_j^{(k)}$ shall be normalized[9]:

$$(\psi_j^{(k)}, \psi_j^{(k)}) = 1 \tag{18}$$

At first we disregard nonorthogonalities:

$$(\psi_j^{(k)}, \psi_{j'}^{(k')}) = \delta_{kk'}\delta_{jj'} \tag{19}$$

Now we form the following linear combinations:

$$\chi_i^{(k)} = \sum_j c_{ij}\psi_j^{(k)}, \tag{20}$$

where c_{ij} are the components of the normalized eigenvectors of the structure matrix. From the theorem that the eigenvectors of a matrix are orthogonal and from Eq. (19) follows

$$(\chi_i^{(k)}, \chi_{i'}^{(k)}) = \delta_{ii'} \tag{21}$$

Now we define the operator $\mathscr{H}$ by the following equation:

$$(\psi_j^{(k)}, \mathscr{H}\psi_{j'}^{(k)}) = (\varepsilon_k + \alpha_{kk})\delta_{jj'} + \beta_{kk}s_{jj'} \tag{22}$$

Then we have

$$(\chi_i^{(k)}, \mathscr{H}\chi_{i'}^{(k)}) = (\varepsilon_k + \alpha_{kk} + \rho_i\beta_{kk})\delta_{ii'} \tag{23}$$

For $k = 2$ the secular problem

$$|(\chi_i^{(k)}, \mathscr{H}\chi_{i'}^{(k)}) - (\chi_i^{(k)}, \chi_{i'}^{(k)})E^{(k)}| = 0 \tag{24}$$

is exactly the secular problem of Hückel's theory. With respect to (23) the linear combinations (20) are the right linear combinations of zeroth order of Hückel's secular problem. The roots of the problem are

$$(E^{(k)} - \varepsilon_k)_i = \alpha_{kk} + \rho_i\beta_{kk} \tag{25}$$

For a value k' of the principal quantum number the linear combinations

$$\chi_i^{(k')} = \sum_j c_{ij}\psi_j^{(k')} \tag{26}$$

diagonalize the respective secular problem belonging to k':

$$|(\chi_i^{(k')}, \mathscr{H}\chi_{i'}^{(k')}) - (\chi_i^{(k)}, \chi_{i'}^{(k')})E^{(k')}| = 0 \tag{27}$$

The roots of this problem are

$$(E^{(k')} - \varepsilon_{k'})_i = \alpha_{k'k'} + \rho_i\beta_{k'k'} \tag{28}$$

Now we assume

$$(\psi_j^{(k)}, \mathscr{H}\psi_{j'}^{(k')}) = \alpha_{kk'}\delta_{jj'} + \beta_{kk'}s_{jj'} \tag{29}$$

That means that also for the combination integrals there will only be interaction between neighbors. From this assumption follows the relation

$$(\chi_i^{(k)}, \mathscr{H}\chi_{i'}^{(k')}) = (\alpha_{kk'} + \rho_i\beta_{kk'})\delta_{ii'} \qquad \text{for} \qquad k \neq k' \qquad (30)$$

Now we write down the nm-dimensional secular problem which belongs to the functions

$$\chi_i^{(k)} \qquad k = 2, 3, \ldots, m \qquad i\colon\ 1, 2, \ldots, n \qquad (31)$$

Because of the non-combination relation (30) this problem is split into n problems, each of them belonging to a certain value of i. With (23) and (30) these problems have the following form:

$$|\alpha_{kk'} + \rho_i\beta_{kk'} + (\varepsilon_k - E^{(i)})\delta_{kk'}| = 0 \qquad i = 1, 2, \ldots, n \qquad (32)$$

We can order the roots $E^{(i)}$ of the problem belonging to i according to their values and use the index r to describe this order. If r is constant $E_r^{(i)}$ is a function of ρ_i:

$$E_r^{(i)} = E_r^{(i)}(\rho_i) \qquad i = 1, 2, \ldots, n \qquad (33)$$

These n values $E_r^{(i)}$ we call the rth band. So we can collect all terms which result from the nm-dimensional problem in a sensible way into bands. We call the function (33) the characteristic function of the band. When the characteristic function is known and when the Hückel numbers for the molecule are known, one can deduce the energy values in a way which is schematically described in Fig. 5. According to (32) the characteristic functions themselves are independent of the special molecule. They are general. The band for $r = 1$ we call the valence band. Hückel's pure $2p$ theory gives as characteristic function of the valence band

$$E_1^{(i)} = \alpha + \rho_i\beta \qquad (34)$$

In the case that $2p$ and $3p$ functions are included, the secular problem (32) is of the second degree and has the form

$$\begin{vmatrix} \alpha_{22} + \rho\beta_{22} + \varepsilon_2 - E & \alpha_{23} + \rho\beta_{23} \\ \alpha_{23} + \rho\beta_{23} & \alpha_{33} + \rho\beta_{33} + \varepsilon_3 - E \end{vmatrix} = 0 \qquad (35)$$

When the Coulomb integrals are relatively small, the problem assumes the form

$$\begin{vmatrix} \rho\beta_{22} + \varepsilon_2 - E & \rho\beta_{23} \\ \rho\beta_{23} & \rho\beta_{33} + \varepsilon_3 - E \end{vmatrix} = 0 \tag{36}$$

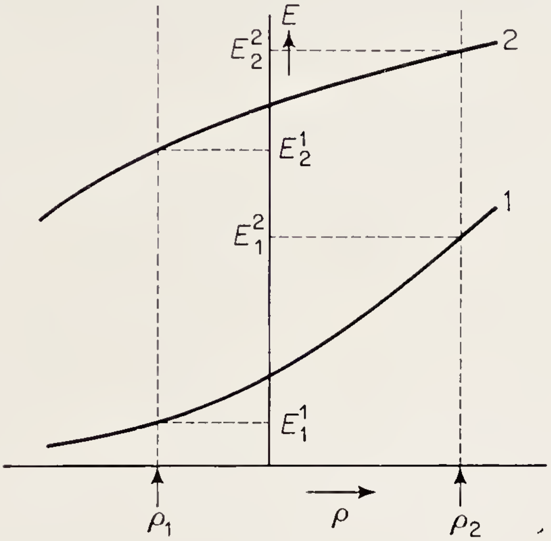


Fig. 5

The solutions of this problem are

$$\begin{aligned} \varepsilon = \tfrac{1}{2}\Bigg\{&[\varepsilon_0 + \rho(\beta_{22} + \beta_{33})] \\ &\pm |[\varepsilon_0 + \rho(\beta_{22} + \beta_{33})]| \left(1 - 4\rho\,\frac{\varepsilon_0\beta_{22} + \rho(\beta_{22}\beta_{33} - \beta_{23}{}^2)}{[\varepsilon_0 + \rho(\beta_{22} + \beta_{33})]^2}\right)^{\frac{1}{2}}\Bigg\} \end{aligned} \tag{37}$$

The meaning of ε_0 and ε is given by

$$\varepsilon_0 = \varepsilon_3 - \varepsilon_2 \qquad \varepsilon = E - \varepsilon_2 \tag{38}$$

From (37) one gets the characteristic function of the valence band if one takes the negative sign.

VI. THE PARAMETERS OF THE THEORY

The characteristic function (37) contains three resonance integrals as parameters. For the evaluation of the characteristic function, ε_3 also has to be known. It is reasonable to take for ε_3 the value where

$$\varepsilon_3 = -E_a/3^2 \tag{39}$$

$E_a = 13.5$ ev is the ionization energy of the hydrogen atom. So ε_0 is approximately 2.7 ev. One can try to deduce the values of the three resonance integrals from the energies of the bonding and the antibonding molecular states of the ethylene molecule. In this way only two parameters can be determined as functions of the third one. The result is shown in Fig. 6. It seems to be difficult to determine a reasonable value for the third parameter, but one can show that the essential results of the theory are practically independent of the value chosen for the third parameter.

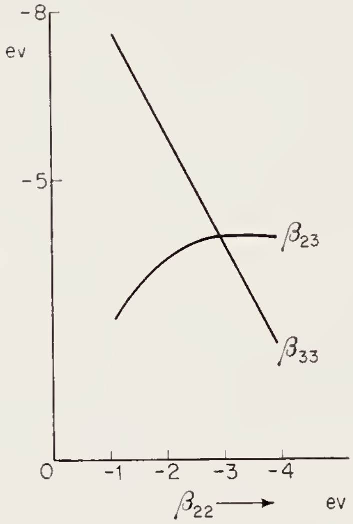


Fig. 6

Figure 7 shows the four curves which one gets for the characteristic function of the valence band if one inserts the values -1, -2, -3, and -4 ev for the parameter β_{22}. It is easily seen that there are only small differences between the four curves. The general type is always the same. And even this type is quite different from the characteristic function which resulted from the Hückel theory.

The main difference between our extended theory and the Hückel theory is that in the Hückel theory the upper and lower halves of the valence band are symmetrical, while in our theory the upper half of the valence band is quite narrow and so the term density in this half of the valence band becomes very high. The energies of the molecular electron states which belong to the upper half of the valence band should be nearly the same.

This result is very important in so far as it gives the explanation of a phenomenon which recently has been detected by Scheibe and coworkers and which could not be explained by existing theories. Scheibe could show that the ionization energies of molecules with π-electron systems from the first excited state have nearly the same value for all molecules of this group, while the ionization energies of these molecules in the ground state are very different for different molecules. Normally, the first excited state of the molecule belongs to an electron configuration which can be built out of the electron configuration belonging to the ground state by shifting one electron from the last occupied molecular state to the first unoccupied state. To this state corresponds a positive Hückel number between 0 and 1.

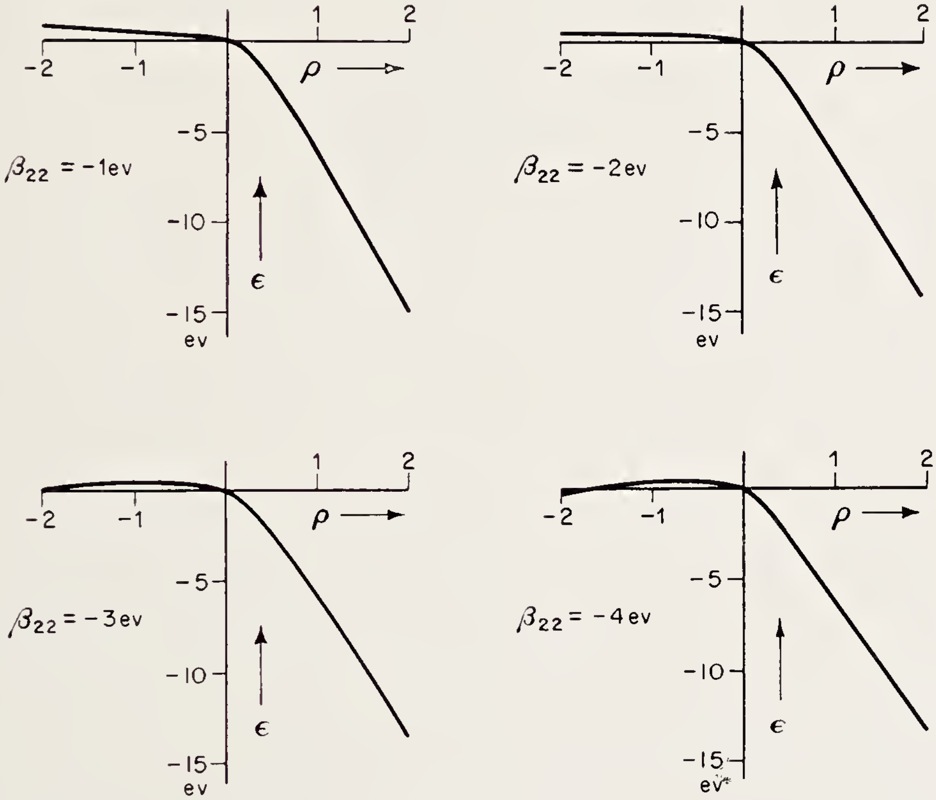


Fig. 7

As we have shown, the corresponding energy value should be nearly independent of the exact value of the Hückel number and so the energy necessary for a removal of the excited electron from this state to the ionization limit should be nearly independent of this value and, therefore, of the molecular species which is considered. This is a reasonable explanation of Scheibe's phenomenon.

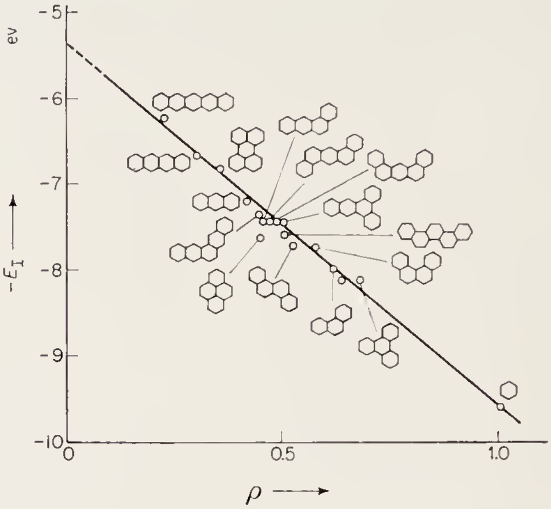


Fig. 8

From (37) it can be seen that the descending branch of the characteristic function for greater values of ρ should become a straight line. This branch of the characteristic function can be determined from empirical values of ionization energies of different molecules in the ground state.[10] Ionization in this case means the removal of an electron from the last occupied electronic state of the molecule. In Fig. 8 the relation between ionization energy and the Hückel number of the last occupied electronic state is shown. With regard to the limited accuracy of the values of the ionization energy, one can state a perfect correspondence between the theory and the empirical facts. From the figure it can be seen that for the typical aromatic C—C distance the characteristic function in the range $0.2 < \rho < 1$ can be represented by the linear function

$$E = -5.4 - 4.2\rho \tag{40}$$

From the difference between the ionization energies of ethylene (10.4 ev) and benzene (9.6 ev), which both correspond to $\rho = 1$, it is to be seen that the descending branch of the characteristic function is different for ethylene and aromatic hydrocarbons. This is in accordance with the fact that the values of the resonance integrals should decrease with increasing distance of the atoms. It can be seen, too, that the energy of the trigonal valence state lies somewhat lower than estimated by Mulliken, van Vleck, and Voge.

VII. ABSORPTION SPECTRA OF AROMATIC HYDROCARBONS

It is interesting to see whether the spectroscopic data about aromatic hydrocarbons fit into the theory. We call the electronic states of the lower half of the valence band $b_1, b_2, \ldots$ and the states of the upper half $l_1, l_2, \ldots$. The spectroscopic ground state of the molecule belongs to the configuration $b_1^2 b_2^2 \ldots b_{(n/2)}^2$. If E_g is the one-electron energy of this configuration, we can write for the energy of the spectroscopic ground state of the molecule

$$E_{1(^1)} = E_g + C' \tag{41}$$

The second singlet state and the first triplet state of the molecule belong to the configuration $b_1^2 b_2^2 \ldots b_{(n/2)}^1 l_1^1$ with "normal" molecules. If E_a means the energy of this configuration, we can write

$$E_{2(^1)} = E_a + C - A, \qquad E_{1(^3)} = E_a + C + A \tag{42}$$

A is an exchange integral. The terms $2(^1)$ and $1(^3)$ in the literature are described by ^1L_a and $^3L_3$. The empirical data[11] show that the difference $E_{2(^1)} - E_{1(^3)}$, which should be twice the exchange integral, is nearly constant within the group of aromatic hydrocarbons. From Eqs. (41) and (42) we calculate the quantity

$$\begin{aligned}[(E_{2(^1)} + E_{1(^3)})/2] - E_{1(^1)} &= (E_a - E_g) + (C - C') \\ &= [E_{l_1} - E_{b_{(n/2)}}] + (C - C') \end{aligned} \tag{43}$$

With regard to the remarkable constancy of A it is very reasonable that the difference $C - C'$ should be constant, too. In Fig. 9 for each hydrocarbon there are seen to be two points. One of them lies above the Hückel number of the last occupied electron state, the second above the Hückel number of the first electron state of the upper half of the band. The points in the right part of the diagram are designed according to the ionization energy of the molecules. This part of the diagram is analogous to Fig. 8.

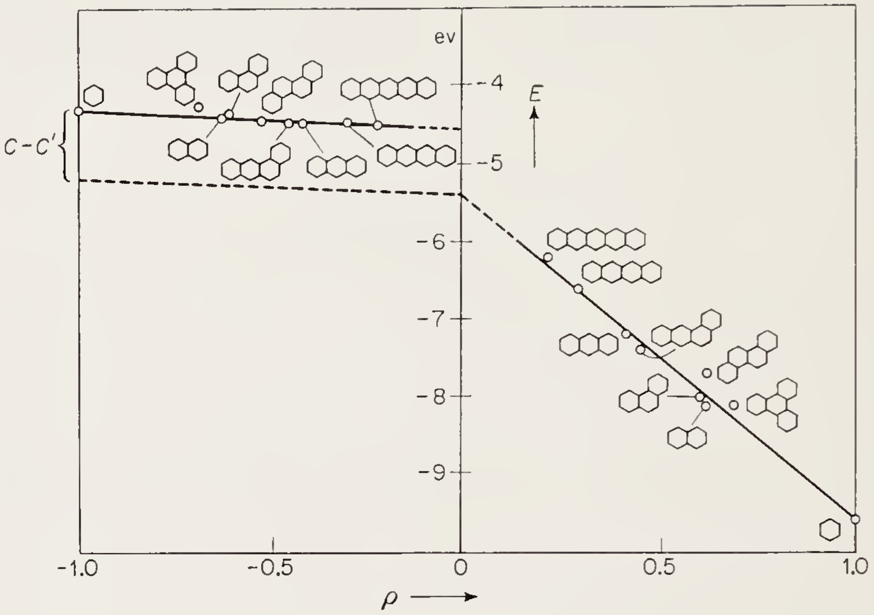
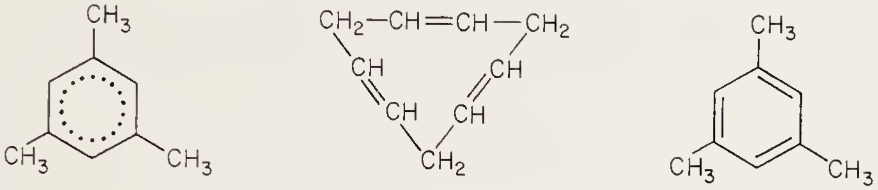


Fig. 9

The difference in height of two corresponding points in the right and left parts of the diagram is the empirical value of the quantity (43). One can easily see that with a value of 0.85 ev for $C - C'$ the spectroscopic data give the characteristic function just in the form demanded by the theory.

VIII. RESONANCE ENERGIES

It is interesting to discuss the problem of how far the theory described here can give a sufficient explanation of empirical resonance-energy values. Unfortunately Hückel's definition of the theoretical resonance energy given in his papers seems to be wrong. Hückel uses the method of valence-bond structure, too. With this method he calculates the following three π-electron energy values (Fig. 10). A and C are the characteristic exchange and Coulomb integrals of the method of valence-bond structures. E_1 is the energy of the ground state of the π-electron system of the mesitylene molecule. E_2 is the sum of the corresponding energies of three nonconjugated ethylene molecules. The value E_3 is to be attributed to a localized Kekule structure of the mesitylene molecule. According to Hückel, only the energy value E_3 corresponds to the energy value which can be calculated from empirical bond-energy constants. Quite consequently he defines the theoretical resonance energy in the following way:

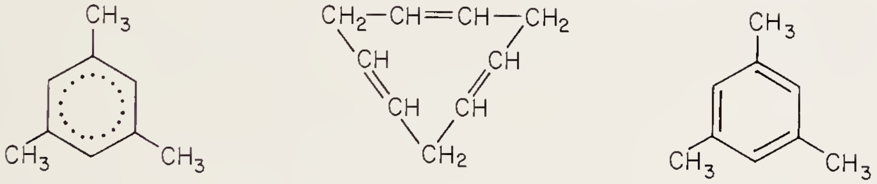


$E_1 = 6C + 2.6A$ $E_2 = 3C + 3A$ $E_3 = 6C + 1.5A$

Fig. 10

$$E_S = E_3 - E_1 = -1.1A \tag{44}$$

We think that this is correct. According to Hückel, the application of the molecular-orbital method to the same problem gives the following results (Fig. 11). E_3 does not exist. The term "localized valency" is not defined in this method. A comparison of the two tables shows that the difference $E_2 - E_1$ is *not* the theoretical resonance energy, but Hückel has used this definition and others have followed him. We think that this is not correct. If δE means the difference between the energy of a localized Kekule structure and E_2, it seems to be correct to put



$E_1 = 6\alpha + 8\beta$ $E_2 = 6\alpha + 6\beta$ ——

Fig. 11

$$E_S = \delta E + (E_2 - E_1) = \delta E - 2\beta \tag{45}$$

In the case we have discussed, the method of valence-bond structures leads to the result

$$\delta E = E_3 - E_2 = 3C - 1.5A \tag{46}$$

Generally this method for a molecule with $n/2$ double bonds and $n/2$ single bonds between double bonds gives

$$E_3 = nC + (n/4)A \tag{47}$$

and

$$E_2 = (n/2)C + (n/2)A \tag{48}$$

So one has the result

$$\delta E = E_3 - E_2 = nE_0, \qquad E_0 = \tfrac{1}{2}(C - \tfrac{1}{2}A) \tag{49}$$

δE, under these circumstances, is proportional to the number of carbon atoms. Certainly this value of δE cannot be taken over directly into the one-electron theory, but we may assume reasonably that δE is proportional to the number of carbon atoms. The factor of proportionality has to be determined empirically. If the positive branch of the characteristic function is sufficiently linear, E can be calculated in a very simple manner. At first we define

$$\sigma = 2\sum_{i=1}^{n/2} \rho(b_i) \tag{50}$$

The positive branch of the characteristic function may be given by

$$E = -A - B\rho \tag{51}$$

Then we have

$$E_1 = -nA - \sigma B \tag{52}$$

Then we have

$$E_S = nE_0 - (nE_{IE} - nA - \sigma B) \tag{53}$$

E_{IE} is the ionization energy of ethylene.

For the group of aromatic hydrocarbons we can use the values

$$A = 5.4 \text{ ev}, \qquad B = 4.2 \text{ ev} \tag{54}$$

Therefore we have finally

$$E_S = nE_0 - (5n - 4.2\sigma) \tag{55}$$

The result of the calculation of E_0 from the empirical resonance energy of the anthracene molecule is

$$E_0 = -0.962 \text{ ev} \tag{56}$$

With this value of E_0 we have calculated some theoretical resonance energies. In Table I they are compared with the empirical values. Besides the case of benzene which apparently plays a singular part in the group of aromatic hydrocarbons, the coincidence is very good. This is an astonishing effect because until now caloric and spectroscopic energy values within the Hückel theory differed by a factor of 3.

TABLE I

	E_S theor., ev	E_S exp., ev
Benzene	2.6	1.8
Naphthalene	3.9	3.3
Anthracene	5.0	5.0
Phenanthrene	5.6	5.6

IX. CHARGE DENSITIES, SELF CONSISTENCY, BOND ORDERS

Gliemann and Weiss have investigated some interesting topics in the extended theory. Their results are described in this section.

The functions which diagonalize the secular equation (32) are linear combinations of the $\chi_i^{(k)}$:

$$\varphi_{il} = \sum_k \Gamma_{il}^{(k)} \chi_i^{(k)} \qquad l = 1, 2, \ldots, m \tag{57}$$

Because of the orthonormality of the $\chi_i^{(k)}$ and because of

$$(\varphi_{il}, \varphi_{il'}) = \delta_{ll'} \tag{58}$$

one gets

$$\sum_k |\Gamma_{il}^{(k)}|^2 = 1 \tag{59}$$

With respect to (20) one sees that the φ_{il} are linear combinations of the atomic functions $\psi_j^{(k)}$ as follows

$$\varphi_{il} = \sum_j c_{ij} \sum_k \Gamma_{il}^{(k)} \psi_j^{(k)} \tag{60}$$

The $\sum_k \Gamma_{il}^{(k)} \psi_j^{(k)}$ can be interpreted as hybrid functions at the jth atom.

Now let us define the mobile charges in the sense of the original definition in Hückel's theory: the charge density at the jth atom produced by an electron in the state φ_{il} may be

$$q_j^{(il)} = \int \varphi_{il}^{\star} \varphi_{il} d\tau_j \tag{61}$$

The integral must be taken over the functions ψ_j. No other functions $\psi_{j'}$ $(j' \neq j)$ contribute to the integral. With (59) follows easily

$$q_j^{(il)} = |c_{ij}|^2 \tag{62}$$

We call N_{il} $(= 0, 1, \text{ or } 2)$ the occupation number of the state φ_{il} and get as the total charge density at atom j

$$q_j = \sum_i \sum_l N_{il} |c_{ij}|^2 \tag{63}$$

Let us suppose that the electrons of a π-electron system occupy only states of the valence band, that means $N_{il} = 0$ for $l \neq 1$. We see

$$q_j = \sum_i N_{i1} |c_{ij}|^2 \tag{64}$$

Especially for the ground state of a neutral, nonradical π-electron system the charge density at atom j is

$$q_j = 2 \sum_{i=1}^{n/2} |c_{ij}|^2 \tag{65}$$

Here we have supposed that the energy of the valence band is a monotonic function of ρ_i with $E_i' > E_i$ for $\rho_i' < \rho_i$ when $i < i'$. In Section X it is shown that the energy in every band is indeed a monotonic function of Hückel's numbers.

The q_j in Eqs. (64) and (65) are the same as in Hückel's theory. We know that the c_{ij} are the components of the normalized eigenvectors of the structure matrix which is defined by the neighboring relations of the carbon atoms only. Therefore we find the charge densities of a π-electron system are—also in the given expansion of Hückel's theory—determined only by the structure of the molecule.

The theory of π-electron systems in our approximation is self-consistent if the total charge density at every atom is one. For alternant hydrocarbons[12] in the ground state this can easily be shown. The following structure matrix belongs to such hydrocarbons

$$\gamma = \left(\begin{array}{c:c} 0 & \gamma_1 \\ \hdashline \gamma_2 & 0 \end{array}\right) \tag{66}$$

The submatrices γ_1 and γ_2 fulfil the relation $\tilde{\gamma}_1 = \gamma_2$.

If γ_1 and γ_2 are quadratic matrices it follows that:

(a) The eigenvalues (that are in our case the Hückel numbers) of (66) lie symmetrically about zero:

$$\rho_i = -\rho_{n-i+1} \tag{67}$$

(b) For the components of the corresponding eigenvectors the relation

$$|c_{ij}| = |c_{n-i+1,j}| \tag{68}$$

holds.

Since the c_{ij} describe a unitary transformation, i.e. besides $\sum_j |c_{ij}|^2 = 1$, also the relation

$$\sum_i |c_{ij}|^2 = 1 \tag{69}$$

is right, it can easily be recognized that therefore the q_j in (65) have the value one. If γ_1 and γ_2 are non-quadratic matrices by similar reasons one finds also that $q_j = 1$. So one sees that the field of an alternant hydrocarbon is self-consistent.

Analogous considerations like those given above for the charge densities lead to the bond orders between the jth and the j'th carbon atom in our extension of Hückle's theory

$$\rho_{jj'} = \sum_i \sum_l N_{il} c_{ij} c_{ij'} \tag{70}$$

If all π electrons are in the valence band (70) reduces to the bond orders of the original Hückel theory

$$\rho_{jj'} = \sum_i N_{i1} c_{ij} c_{ij'} \tag{71}$$

Charge densities and bond orders can also be represented by certain differential quotients. Starting with

$$E_l^{(i)} = \frac{\int \varphi_{il}^\star \mathscr{H} \varphi_{il} d\tau}{\int \varphi_{il}^\star \varphi_{il} d\tau} \tag{72}$$

one gets

$$E_l^{(i)} = \sum_{j=1}^{m} |c_{ij}|^2 \, {}^{l}\mathrm{A}_j + 2 \sum\sum_{j<j'} c_{ij}^\star c_{ij'} \, {}^{l}\text{Б}_{jj'} \tag{73}$$

with

$$\begin{aligned} {}^{l}\mathrm{A}_j &= \sum_{k}\sum_{k'} \Gamma_l^{(k)} \Gamma_l^{(k')} \alpha_{j,kk'} \\ {}^{l}\text{Б}_{jj'} &= \sum_{k}\sum_{k'} \Gamma_l^{(k)} \Gamma_l^{(k)} \beta_{jj',kk'} s_{jj'} \end{aligned} \tag{74}$$

and

$$\begin{aligned} (\psi_j^{(k)}, \mathscr{H} \psi_j^{(k')}) &= \alpha_{j,kk'} \\ (\psi_j^{(k)}, \mathscr{H} \psi_{j'}^{(k')}) &= \beta_{jj',kk'} \end{aligned} \tag{75}$$

With the definition of the energy of these π electrons occupying the lth band

$$\mathcal{E}_l = \sum_{i=1}^{n} N_{il} E_l^{(i)} \tag{76}$$

one can show that for the charge densities and the bond orders holds

$$\begin{aligned} q_j &= \sum_{l=1}^{n} (\partial \mathcal{E}_l / \partial\, {}^{l}\mathrm{A}_j)_{\Delta=0} \\ p_{jj'} &= \sum_{l=1}^{n} (\partial \mathcal{E}_l / \partial\, {}^{l}\text{Б}_{jj'})_{\Delta=0} \end{aligned} \tag{77}$$

Neglecting all $\psi^{(k')}$ with $k' \neq 2$ naturally the q_j and the $p_{jj'}$ in (77) reduce to the q_j and $p_{jj'}$ given by Coulson and coworkers[13] for Hückel's scheme.

Similar considerations are applicable to the determination of the distinct polarizabilities and to the integral representation of the energies and the quantities p, q, and π given for Hückel's theory by Coulson and coworkers, also.

X. QUANTITATIVE ANALYSIS OF THE PARAMETERS

Quite recently E. Ruch has made two contributions to the extended theory which we have described. His results are still unpublished. These contributions are discussed in this and the following section.

If one wants to develop a semiquantitative theory of the resonance integrals $\beta_{kk'}$ it suffices to study the case of ethylene because the resonance integrals used in the extended theory are supposed to be independent of the number of atoms in the molecule.

The full Hamiltonian for each π electron in the ethylene molecule has the following form

$$\mathscr{H} = T - V_{\mathrm{a}} - V_{\mathrm{b}} + V_{\mathrm{a}}' + V_{\mathrm{b}}' \tag{78}$$

T is the operator of the kinetic energy of the electron, V_{a} and V_{b} are the potential energies of an electron against the cores of the atoms a and b. $V_{\mathrm{a}}' + V_{\mathrm{b}}'$ is a shielding potential energy which can be separated in two parts, each belonging to one of the two atoms.

It is reasonable to make some statements about the form of the shielding potential:

1. If one of the two π electrons has a great distance from the molecule the second π electron shields the charge of each carbon atom from 1 to $\frac{1}{2}$.

2. This shielding decreases with decreasing distance of the first electron.

3. If the electron is in the neighborhood of the core, the shielding potential energy becomes constant.

Schematically these properties can be described in the following way:

$$\begin{array}{llcl} & \nearrow (V_{\mathrm{a}}/2) & & r_{\mathrm{a}} \to \infty \\ (V_{\mathrm{a}}/2) \geq V_{\mathrm{a}}' & & \text{for} & \\ & \searrow \text{const} & & r_{\mathrm{a}} \to 0 \\ & \nearrow (V_{\mathrm{b}}/2) & & r_{\mathrm{b}} \to \infty \\ (V_{\mathrm{b}}/2) \geq V_{\mathrm{b}}' & & \text{for} & \\ & \searrow \text{const} & & r_{\mathrm{b}} \to 0 \end{array} \tag{79}$$

It is convenient to write

$$\begin{aligned} V_{\mathrm{a}}' &= (V_{\mathrm{a}}/2) + V_{\mathrm{a}}'' \\ V_{\mathrm{b}}' &= (V_{\mathrm{b}}/2) + V_{\mathrm{b}}'' \end{aligned} \tag{80}$$

Then we have

$$\begin{array}{llll} 0 \geq V_{\mathrm{a}}'' & \begin{array}{l} \nearrow 0 \\ \searrow -(V_{\mathrm{a}}/2) + \text{const} \end{array} & \text{for} & \begin{array}{l} r_{\mathrm{a}} \to \infty \\ r_{\mathrm{a}} \to 0 \end{array} \\ 0 \geq V_{\mathrm{b}}'' & \begin{array}{l} \nearrow 0 \\ \searrow -(V_{\mathrm{b}}/2) + \text{const} \end{array} & \text{for} & \begin{array}{l} r_{\mathrm{b}} \to \infty \\ r_{\mathrm{b}} \to 0 \end{array} \end{array} \tag{81}$$

V_{a}'' and V_{b}'' are essentially different from zero only in the neighborhood of the respective core.

The resonance integral with two equal indices is defined by

$$\begin{aligned} \beta_{kk} &= (\psi_{\mathrm{a}}^{(k)}, [-V_{\mathrm{a}} + V_{\mathrm{a}}' + V_{\mathrm{b}}']\psi_{\mathrm{b}}^{(k)}) \\ &= (\psi_{\mathrm{a}}^{(k)}, [-(V_{\mathrm{a}}/2) + (V_{\mathrm{b}}/2)]\psi_{\mathrm{b}}^{(k)}) + (\psi_{\mathrm{a}}^{(k)}, [V_{\mathrm{a}}'' + V_{\mathrm{b}}'']\psi_{\mathrm{b}}^{(k)}) \end{aligned} \tag{82}$$

From symmetry considerations follows

$$(\psi_{\mathrm{a}}^{(k)}, [-(V_{\mathrm{a}}/2) + (V_{\mathrm{b}}/2)]\psi_{\mathrm{b}}^{(k)}) = 0 \tag{83}$$

So with regard to (81) we get

$$\beta_{kk} = (\psi_{\mathrm{a}}^{(k)}, [V_{\mathrm{a}}'' + V_{\mathrm{b}}'']\psi_{\mathrm{b}}^{(k)}) < 0 \tag{84}$$

For the case of different upper indices we have the two following representations:

$$\begin{aligned} (\psi_{\mathrm{a}}^{(k)}, \mathscr{H}\psi_{\mathrm{b}}^{(k')}) &= S_{kk'}\varepsilon_l + (\psi_{\mathrm{a}}^{(k)}, [-(V_{\mathrm{a}}/2) + (V_{\mathrm{b}}/2)]\psi_{\mathrm{b}}^{(k')}) \\ &\quad + (\psi_{\mathrm{a}}^{(k)}, [V_{\mathrm{a}}'' + V_{\mathrm{b}}'']\psi_{\mathrm{b}}^{(k')}) \\ (\psi_{\mathrm{a}}^{(k')}, \mathscr{H}\psi_{\mathrm{b}}^{(k)}) &= S_{kk'}\varepsilon_k + (\psi_{\mathrm{a}}^{(k')}, [-(V_{\mathrm{a}}/2) + (V_{\mathrm{b}}/2)]\psi_{\mathrm{b}}^{(k)}) \\ &\quad + (\psi_{\mathrm{a}}^{(k')}, [V_{\mathrm{a}}'' + V_{\mathrm{b}}'']\psi_{\mathrm{b}}^{(k)}) \end{aligned} \tag{85}$$

Because of the self-adjoint character of $\mathscr{H}$ and from symmetry considerations it follows that the left sides of these two equations are equal. The same is true for the last integrals on the right side. By exchange of a and b one can see that in both equations the two remaining integrals differ only by their sign. By subtraction one gets

$$\begin{aligned} &(\psi_{\mathrm{a}}^{(k)}, [-(V_{\mathrm{a}}/2) + (V_{\mathrm{b}}/2)]\psi_{\mathrm{b}}^{(k')}) \\ &\qquad = -(\psi_{\mathrm{a}}^{(k')}, [-(V_{\mathrm{a}}/2) + (V_{\mathrm{b}}/2)]\psi_{\mathrm{b}}^{(k)}) = \tfrac{1}{2}S_{kk'}(\varepsilon_k - \varepsilon_l) \\ &(\psi_{\mathrm{a}}^{(k)}, \mathscr{H}\psi_{\mathrm{b}}^{(k')}) \\ &\qquad = S_{kk'}[(\varepsilon_k - \varepsilon_l)/2] + (\psi_{\mathrm{a}}^{(k)}, [V_{\mathrm{a}}'' + V_{\mathrm{b}}'']\psi_{\mathrm{b}}^{(k')}) \end{aligned} \tag{86}$$

This leads to

$$\beta_{kk'} = (\psi_{\mathrm{a}}^{(k)}, [V_{\mathrm{a}}'' + V_{\mathrm{b}}'']\psi_{\mathrm{b}}^{(k')}) < 0 \tag{87}$$

Ruch has shown that with a reasonable choice of V_{a} and V_{b} one can get values for the resonance integrals which are well in accord with the values determined empirically above. Nevertheless it is possible to draw the general discussion further. From Eq. (86) it follows that it is reasonable to neglect the integral

$$(\psi_{\mathrm{a}}^{(k)}, [-(V_{\mathrm{a}}/2) + (V_{\mathrm{b}}/2)]\psi_{\mathrm{b}}^{(k')}) \tag{88}$$

if non-orthogonality is neglected in the whole theory. It is easily seen that there is only a small difference between (88) and the integral

$$\varepsilon_{kk'} = (\psi_{\mathrm{a}}^{(k)}, [V_{\mathrm{a}}'' - V_{\mathrm{b}}'']\psi_{\mathrm{b}}^{(k')}) \tag{89}$$

We put

$$\beta_{kk'} \approx \beta_{kk'} + \varepsilon_{kk'} = 2(\psi_{\mathrm{a}}^{(k)}, V_{\mathrm{a}}''\psi_{\mathrm{b}}^{(k')}) \tag{90}$$

and

$$\beta_{kk'} \approx \beta_{kk'} - \varepsilon_{kl} = 2(\psi_{\mathrm{a}}^{(k')}, V_{\mathrm{a}}''\psi_{\mathrm{b}}^{(k)}) \tag{91}$$

So we have

$$\beta_{kk'}^2 \approx \beta_{kk'}^2 - \varepsilon_{kl}^2 = 4(\psi_{\mathrm{a}}^{(k)}, V_{\mathrm{a}}''\psi_{\mathrm{b}}^{(k')})(\psi_{\mathrm{a}}^{(k')}, V_{\mathrm{a}}''\psi_{\mathrm{b}}^{(k)}) \tag{92}$$

Without any difficulty one can deduce

$$\beta_{kk} = 2(\psi_{\mathrm{a}}^{(k)}, V_{\mathrm{a}}''\psi_{\mathrm{b}}^{(k)}) \tag{93}$$

and so

$$\beta_{kk}\beta_{k'k'} = 4(\psi_{\mathrm{a}}^{(k)}, V_{\mathrm{a}}''\psi_{\mathrm{b}}^{(k)})(\psi_{\mathrm{a}}^{(k')}, V_{\mathrm{a}}''\psi_{\mathrm{b}}^{(k')}) \tag{94}$$

The p functions $\psi_{\mathrm{b}}^{(k)}$ can be represented by $\sin\vartheta_{\mathrm{b}}\,\phi(\varphi)R^k(r_{\mathrm{b}})$. ϑ_{b} is the angle between r_{b} and the line joining the nuclei. φ is the angle round this line. Therefore the values of the function $V_{\mathrm{a}}''\sin\vartheta_{\mathrm{b}}$ are essentially different from zero in the region described in Fig. 12. Therefore it is possible to put

$$(\psi_{\mathrm{a}}^{(k)}, V_{\mathrm{a}}''\psi_{\mathrm{b}}^{(k')}) = R^{k'}(\overline{r_{\mathrm{b}}})(\psi_{\mathrm{a}}^{(k)}, V_{\mathrm{a}}''\sin\vartheta_{\mathrm{b}}\,\phi(\varphi)) \tag{95}$$

$\overline{r_{\mathrm{b}}}$ means an averaged r value independent from k and l. With this approximation one gets

$$\beta_{kk'}^2 = \beta_{kk}\beta_{k'k'} \tag{96}$$

The values of the resonance integrals, which were determined from empirical data are in good agreement with this rule of the geometric mean.

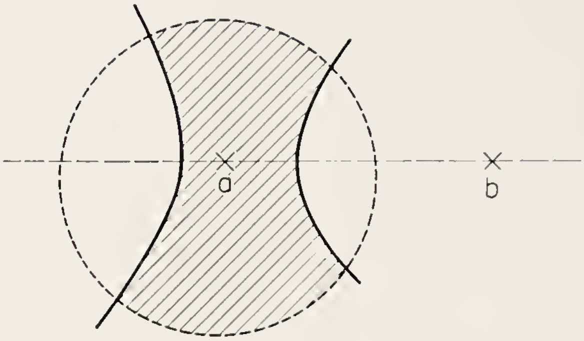


Fig. 12

XI. CONSEQUENCES OF THE RULE OF GEOMETRIC MEAN

The secular determinant

$$\mathrm{Det} = \begin{vmatrix} \varepsilon_2 + \rho\beta_{22} - \lambda & \rho\beta_{23} & \cdots \\ \rho\beta_{32} & \varepsilon_3 + \rho\beta_{33} - \lambda & \cdots \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{vmatrix} \tag{97}$$

is of the $(n - l)$th degree in λ and of the $(n - l)$th degree in ρ. It is possible to write

$$\mathrm{Det} \equiv P(\lambda) + \rho Q(\lambda) + \rho^2 Q_2(\lambda) + \rho^3 Q_3(\lambda) + \ldots = 0 \tag{98}$$

with

$$P(\lambda) = \Pi(\varepsilon_\nu - \lambda) \tag{99}$$

and

$$Q(\lambda) = \beta_{22}(\varepsilon_3 - \lambda)(\varepsilon_4 - \lambda) \ldots + \beta_{33}(\varepsilon_2 - \lambda)(\varepsilon_4 - \lambda) \ldots + \ldots \tag{100}$$

The following $Q_r(\lambda)$ are a sum of all $\binom{n-1}{r}$ products ${}^{(r)}\Pi(\varepsilon_\nu - \lambda)$ which one can get through elimination of r factors out of $\Pi(\varepsilon_\nu - \lambda)$ and which are multiplied with coefficients taken from the matrix $\{\beta\mu\nu\}$. The coefficient of such a product ${}^{(r)}\Pi(\varepsilon_\nu - \lambda)$ is just the subdeterminant of the matrix $\{\beta\mu\nu\}$ which has been constructed by elimination of all rows and columns of such numbers which have not been eliminated in the product ${}^{(r)}\Pi(\varepsilon_\nu - \lambda)$. In Eq. (98) ρ^2 and all higher powers of ρ are multiplied with subdeterminants which lie symmetrical to the principal diagonal. By putting

$$\beta_{kk'} = -(\beta_{kk})^{\frac{1}{2}}(\beta_{k'k'})^{\frac{1}{2}} \tag{101}$$

one can show easily that these subdeterminants are equal to zero. So the secular problem gets the following form:

$$P(\lambda) + \rho Q(\lambda) = 0 \tag{102}$$

We are interested in λ as function of ρ. We divide by ρ^m and go to the limit $\rho \to \infty$. So we get

$$(-\lambda/\rho)^{m-1} + (-\lambda/\rho)^{m-2}\sum_\nu \beta_{\nu\nu} = 0 \tag{103}$$

with the solutions

$$(\lambda/\rho)_{2,3,\cdots,m-1} = 0, \qquad (\lambda/\rho)_m = \sum_\nu \beta_{\nu\nu} \tag{104}$$

That means that we shall have $n - 2$ horizontal asymptotes and one decreasing asymptote. The equation of the decreasing asymptote can be determined explicity. It is

$$\eta = (\Sigma\varepsilon_\nu\beta_{\nu\nu}/\Sigma\beta_{\nu\nu}) + \Sigma\beta_{\nu\nu}\rho \tag{105}$$

The positions of the horizontal asymptotes are determined by the roots of the equation

$$Q(\lambda) = 0 \tag{106}$$

From (100) one can see that these roots always lie between ε_ν and $\varepsilon_{\nu+1}$. All branches cross the energy axis at the respective energy values ε_ν. Therefore the derivatives of these branches at the point $\rho = 0$ have the values

$$(d\lambda/d\rho)_{\rho=0} = \beta_{\nu\nu} \tag{107}$$

They are all negative. For given λ, Eq. (102) is a linear equation in ρ with one and only one solution. Therefore the different branches cannot show maxima or minima. In consequence it follows that between ε_ν and $\varepsilon_{\nu+1}$ we have one and only one asymptote. The whole system of characteristic functions is represented in Fig. 13.

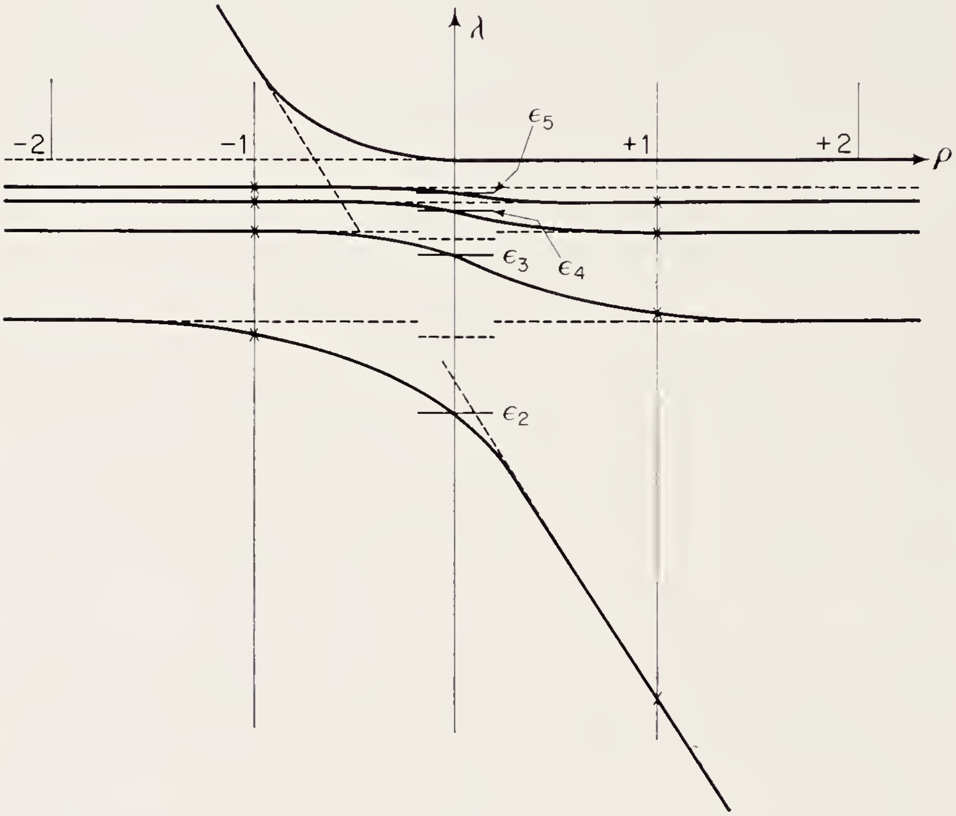


Fig. 13

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SPECTROSCOPY OF TRANSITION-GROUP COMPLEXES

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I. INTRODUCTION

In the decade 1950–1959, the experimental data available on visible and near-ultraviolet absorption spectra of complexes of the transition group elements have been extended enormously, and their theoretical interpretation has made progress such as would not have been believed possible in 1950. However, this area of inorganic chemistry has developed a division as does most physics: that between the experimental and the theoretical. Progress in both areas is impeded because of the division and the lack of cooperation and communication.

Another traditional division line in university teaching is also harmful: that between physics and chemistry. The two most conspicuous failures of classical physics (i.e., Newton's mechanics and Maxwell's electromagnetic theory) were that the chemical valency forces (their selectivity of different atoms and their saturation properties) and the atomic spectral lines (the absorption and emission by gaseous atoms of very distinct sets of exceedingly narrow wave number ranges) were incomprehensible. The evolution of quantum mechanics has by no means reduced chemistry to some obscure subdivision of physics, but, rather, chemistry and atomic spectroscopy undermined centuries of oversimplification. However, the physicists studying electron clouds around 1930 retired from the subject, attracted by nuclei, especially since 1939, and they left a very large field unoccupied until some chemists recently became interested in electronic systems.

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At the same time, a series of superstitions invaded chemical textbooks with highly dubious explanations of chemical bonding.

Actually, the recent studies of transition-group spectra have shown that two different models cherished by many theorists—the electrostatic ligand field model and the valency-bond description (more specifically, the Pauling hybridization theory)—cannot be applied to the observed distribution of energy levels. On the other hand, the molecular orbital (M.O.) configurations give an excellent classification of all energy levels of all complexes; and a unified description is obtained of all polyatomic molecules.

This unification is a surprise to most chemists, they being accustomed to a division of compounds into those having mainly ionic and those having mainly covalent bonding. The M.O. theory is able to explain exactly in what way this distinction is a gradual one, evolving through a continuous series of intermediate cases. It is not only the spectroscopic properties which can be explained by M.O. theory, but also, for instance, magnetochemical properties. The reason for the paramagnetism of O_2, MnO_4^{3-}, $Cr(H_2O)_6^{3+}$, $Ni(NH_3)_6^{2+}$, $ReCl_6^{2-}$, and IrF_6 is essentially the same, i.e., the presence of a half-filled set of M.O. having the same energy.

It has been argued by many physicists and chemists that the electrostatic model is, nevertheless, a satisfactory approximation to the description of the transition-group complexes. However, this argument is only based on the phenomenological introduction of M.O. energy differences and interelectronic repulsion parameters in a semiempirical version of the electrostatic model.

This is not the place to expose the parts of quantum mechanics and group theory used in M.O. theory, since many excellent textbooks exist.[54,89] However, many new examples of how to use this mathematical technique in the description of actual compounds will be given. We may recall that the wave function Ψ for q electrons in a many-electron system is a function of $4q$ variables: three space-variables, and one spin-variable of each electron. Since observables in electron systems do not seem to occur which depend on the relative position of more than two electrons at a time (while three-particle forces perhaps occur in nuclei), the wave function Ψ for three or more electrons is actually more complicated than is needed for the calculation of any interesting property.

This is a rather weak point of present quantum mechanics, since the history of physics is crowded with theories which were abandoned because they supposed redundant information which cannot be experimentally supplied.

As Löwdin[82,173,174] has pointed out, the first- and second-order density matrices are the only quantities needed for knowing the energy levels and all other observables of a many-electron system. In the second-order density matrix, the relative distance between the electrons, taken a pair at a time, decides the size of the interelectronic repulsion energy. However, unfortunately, it has not yet been possible to identify directly the second-order density matrices corresponding to anti-symmetrized Ψ, nor to apply the variation principle of minimum energy.

A. Configurations and Orbitals

Both in atomic spectroscopy (describing gaseous atoms and ions sufficiently isolated from each other to be considered as free) and in M.O. theory, the approximation of *configurations* is introduced. In this approximation, each electron has an orbital ψ, and each orbital may contain zero, one, or two electrons (with opposite spin-directions). However, in atoms and in molecules having a sufficiently high symmetry, systematically degenerate sets of orbitals may occur. In the case of such a partly filled set of orbitals, more than one energy level is often produced. The main reason for this is the interelectronic repulsion between the electrons in the degenerate set, which may correspond to different second-order density matrices. Hence, the configuration with a partly filled set of orbitals is split into several multiplet terms. In heavier atoms, where a very strong electric field exists near the nuclei, another effect of electrodynamic (magnetic) interactions becomes conspicuous, and the multiplet terms split themselves up into several components.

We are using, with Mulliken, lower case letters for denoting the quantum numbers of orbitals and capital letters for quantum numbers of the more-electron systems. The type of these quantum numbers depends on the symmetry of the nuclear distribution of the system considered. The case of atomic spectroscopy is thus approximated by the highest symmetry possible—the spherical symmetry around a single, very, very small, nucleus.

In molecules, the presence of several nuclei degrades the spherical symmetry to lower symmetries. Among the relatively higher symmetries often discussed are:

1. Linear symmetry with a center of inversion ($D_{\infty h}$) as exemplified by the homonuclear, diatomic[97] molecules of H_2 and by linear, triatomic molecules such as CO_2 and UO_2^{2+}.
2. Linear symmetry without a center of inversion ($C_{\infty v}$) as exemplified by heteronuclear, diatomic molecules such as HF and by linear, triatomic molecules such as NNO and SCN^-.
3. Octahedral symmetry with a center of inversion (O_h) as exemplified by many metal complexes, MX_6, where a central atom M is equally bound to six ligands X.
4. Tetrahedral symmetry without a center of inversion (T_d) as exemplified by CH_4, NH_4^+, and many metal complexes such as $CoCl_4^{2-}$ or MnO_4^-.
5. Tetragonal symmetry with a center of inversion (D_{4h}) as exemplified by square-planar metal complexes such as $PdCl_4^{2-}$ and $PtBr_4^{2-}$.

Group theory tells us the conditions for energies to be invariant under special rotations and other group-theoretical operations which do not change the physical conditions of the systems. It is not possible to give an unambiguous list of decreasing symmetries. Thus, the first two symmetries given above permit a rotation about an arbitrarily small or large angle, but only around one axis in space. On the other hand, the octahedral symmetry permits only a finite number of rotation types (90°, 120°, and 180° around different axes), but the three axes of a Cartesian coordinate system will be equivalent in octahedral symmetry. There is a close connection between these operations and the existence of degenerate orbitals ψ in a given symmetry.

The theory of the hydrogen atom, containing one nucleus and one electron, is elaborated in many textbooks. In the more general case of a many-electron system with spherical symmetry, the approximation of configurations introduces one-electron functions

$$\psi = A_l(x,y,z) \cdot R_{nl}(r)/r \tag{1}$$

with

$$x^2 + y^2 + z^2 = r^2,$$

the product of the hydrogen-like angular functions A_l and the radial function R_{nl} (with R_{nl}^2 indicating the electron density per spherical shell at r). It must be emphasized that R_{nl} is *not* hydrogen-like, but is determined in each atom or gaseous ion by the *central field*, which is essentially the spherically symmetrical average of the repulsion from the other electrons added to the attractive potential from the nucleus. Hartree[91] describes the calculation of such radial functions from Schrödinger's equation by numerical integration.

The angular functions A_l can be classified by a quantum number l assuming as values non-negative integers:

$$\begin{array}{ccccccccc} l = & 0 & 1 & 2 & 3 & 4 & 5 & \cdots \\ & s & p & d & f & g & h & \cdots \end{array} \tag{2}$$

For historical reasons, atomic spectroscopists use the letter symbols given in the second row. Each angular function can be written as a linear combination of homogeneous polynomials A_p in the Cartesian variables

$$A_p = x^a y^b z^c / r^l \tag{3}$$

with

$$a + b + c = l$$

Thus, there is only one polynomial possible for $l = 0$, viz., a constant, which we shall call 1, since in the following we neglect normalization constants. For $l = 1$, three polynomials are possible, $x/r, y/r$, and z/r. For $l = 2$, we find only five, and not six, polynomials, which can be chosen:

$$\begin{array}{ccc} xy/r^2 & xz/r^2 & yz/r^2 \\ (x^2 - y^2)/r^2 & & (2z^2 - x^2 - y^2)/r^2 \end{array} \tag{4}$$

The reason for the restriction to five polynomials is that x^2, y^2, and z^2 are not linearly independent, since $(x^2 + y^2 + z^2)/r^2$ is another way of writing 1. In general, only $(2l + 1)$ linearly independent polynomials will be possible for each value of l. For higher values of l, they tend to become very complicated. (See Von der Lage and Bethe's cubic harmonics.[252])

For a given value of l, an infinite series of radial functions R_{nl} is possible. However, they can be arranged according to increasing energy by use of the quantum number n, a positive integer larger than l. The number of values of finite r, where the radial function is zero where it has a node, is $n - l$ including the nucleus at $r = 0$. It is common practice to write n as a number before the l letters of Eq. (2), and it is true that the energy increases with l for a given n:

$$1s < 2s < 2p; \quad 3s < 3p < 3d; \quad 4s < 4p < 4d < 4f; \quad 5s < \cdots$$

Whether the energy is highest for an orbital with low n and high l or for another orbital with higher n and lower l is strongly dependent on the ionic charge z and atomic number Z. Thus, the ground states of most neutral atoms of the first transition group contain two or one 4s electrons besides the $3d$ electrons, while the ions with the charge $z = +2$ have all the electrons outside the argon core placed in the partly filled $3d$ shell in their ground state, and the $4s$ electrons appear only in highly excited configurations.

According to the principle of electroneutrality, we cannot expect the conditions of a transition group atom in a chemical compound to correspond exactly to those of an ionic charge equal to the oxidation number (+3 in $Cr(H_2O)_6^{3+}$, +6 in IrF_6, etc.). We shall later discuss in what way the covalent bonding influences the charge distributions, and we shall conclude that the number of electrons in the partly filled shell, at least in a molecule or complex ion containing only one metal atom, actually has a very sensible, physical significance. Furthermore, it is possible as a fair approximation to describe the partly filled shell as $3d$, $4d$, or $5d$ in the three ordinary transition groups, $4f$ in the lanthanides (the rare earths), and $5f$ in the actinides (or uranides). Incidentally, no complex is known with more than one partly filled shell in the ground state, and a large number among the excited states contain the same configuration d^q or f^q as the ground state (the superscript q indicates the number of electrons).

B. Interelectronic Repulsion Parameters

In the Russell–Saunders approximation, considering electrostatic but neglecting electrodynamic effects, the energy levels of a given configuration can be assembled in (multiplet) terms characterized by the quantum numbers L of orbital angular momentum and S of the total spin. With Mulliken, we use capital letters for the quantum numbers of more-electron systems and lower case letters for the individual orbitals. If the gaseous atom or ion contains only one partly filled shell with only one electron (or $4l + 1$ electrons, i.e., a "hole" in the filled n,l shell which may accommodate $2(2l + 1)$ electrons), only one term arises, with $L = l$ and $S = \frac{1}{2}$. In spectroscopic nomenclature, the terms are denoted ${}^{2S+1}L$ with symbols $S, P, D, F, G, \cdots$ for $L = 0, 1, \cdots$ in analogy with Eq. (2). Two electrons (or $4l$ electrons) in a partly filled shell produce a series of terms with $S = 1$ (triplets) and $S = 0$ (singlets).

$$ {}^1S,\ {}^3P,\ {}^1D,\ {}^3F,\ {}^1G,\ \cdots,\ {}^3(2l-1),\ {}^1(2l) \tag{5}$$

Already three electrons in a partly filled shell may introduce considerable complications. While p^3 corresponds to ${}^4S$, ${}^2D$, and ${}^2P$, d^3 comprises the terms ${}^4F$, ${}^4P$, ${}^2P$, ${}^2D$, ${}^2D'$, ${}^2F$, and ${}^2G$. We remark here that more than one term of the same configuration may exhibit the same combination of L and S. This becomes a very common phenomenon in f^q. The half-filled shell d^5 corresponds to ${}^6S$, ${}^4G$, ${}^4D$, ${}^4P$, ${}^4F$ and not less than eleven doublets ($S = \frac{1}{2}$).

In the theory of pure configurations, the physical reason for the energy difference between different terms is that even with the same radial function in Eq. (1) (and hence, the same kinetic energy and the same potential energy in the central field, i.e., the attraction by the nucleus and the repulsion from the closed shells), the average value of the mutual distance r_{12} between electrons in the partly filled shell (or more appropriately, the average of $1/r_{12}$) may vary according to the distribution of these electrons on the degenerate orbitals with different angular function A_l in Eq. (1). These energy differences can be expressed[37] as linear combinations of the interelectronic repulsion energy integrals F^0, F^2, F^4, F^6, $\cdot \cdot \cdot$, F^{2l}. The coefficients in these linear combinations are obtained by integration over the angular functions, while the parameters F^k themselves are obtained by radial integration.

For two isomorphous radial functions R_{nl} (having the same "shape," i.e., related by a pure scaling factor in the variable r), each of the F^k integrals are proportional to the average value $\langle r^{-1} \rangle$ of the reciprocal distance of the electron from the nucleus, and they are a slowly decreasing function of k. Thus, it is possible with some approximation to calculate $\langle r^{-1} \rangle$ from the observed values[126] of F^k. The coefficient of F^0 is $q(q-1)/2$ for all terms of a given configuration l^q and is therefore comparable to the central field contributions to the energy.

As Racah[214] has pointed out it is often practical to form linear combinations of the remaining l parameters; thus for d electrons

$$B = (1/49)F^2 - (5/441)F^4 \qquad \text{and} \qquad C = (5/63)F^4 \tag{6}$$

and, in the case of f electrons, for instance,

$$E^3 = (1/135)F^2 + (2/1089)F^4 - (175/42471)F^6 \tag{7}$$

Among the advantages of Eqs. (6) and (7) are that the energy differences between terms with the maximum value ($= q/2$ for $q \leqslant 2l + 1$) of S are simple multiples of B and E^3, respectively. (The reader is warned that many authors use parameters F_k defined, e.g., for d electrons by $49F_2 = F^2$ and $441F_4 = F^4$, obtaining simpler coefficients in the energy expressions.)

There is no general rule for the relative order of L,S terms of a given configuration, though low values of L and S in most cases have rather high energies of interelectronic repulsion. However, Hund's rule seems to be generally valid that the lowest term of a configuration with one partly filled shell has the maximum value of S, and among those terms, the maximum value of L.

It is possible to apply the theory of pure configurations in two ways: in a "strong" sense or in a "weak" sense. In the strong sense, the integrals F^k can be calculated from the Hartree–Fock radial functions and then compared with experiment, while in the weak sense, F^k are considered as phenomenological parameters which are fitted to the observed energy levels. However, it is reasonable[119,126] to maintain rather severe conditions on the ratios such as F^2/F^4 which are quite invariant with the form of the radial function. As found by Appel[134] and Watson[254,255], the strong-sense calculations imply values of F^k some 60 to 10% larger than the observed values, the deviations being smaller for large ionic charges. Recent investigations of the neutron diffraction of manganese(II) compounds[62,256] seem to indicate that the deviation is not caused by the actual radial function of gaseous Mn^{2+} having a smaller $\langle 1/r \rangle$ than the Hartree–Fock calculation, but is caused by more subtle effects of electronic correlation, i.e., that the actual wave function and hence its second-order density matrix does not exactly correspond to Slater's definition[37] of a pure configuration constructed from orbitals such as Eq. (1).

In atoms with high atomic numbers, the electrodynamic (magnetic and relativistic) effects are no longer negligible, and the L,S terms of the Russell–Saunders approximation are strongly split. The individual energy levels are now characterized by the quantum number J, and a given term contributes the levels with $J = L + S, L + S - 1, L + S - 2, \cdot\cdot\cdot, |L - S|$. In the cases in which the terms can still be recognized, the levels are written $^{2S+1}L_J$. For instance, the two adjacent levels which are the excited states of the two strong, yellow lines of sodium are $^2P_{1/2}$ and $^2P_{3/2}$ of the excited configuration $1s^22s^22p^63p$, the first ten electrons being in the neon shells. However, the quantum numbers S and L often become strongly mixed and no longer have defined values. Thus the four levels $^3P_0$, $^3P_1$, $^3P_2$, and $^1P_1$ of the excited configuration

$$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s6p$$

(usually called $6s6p$, omitting the closed shells) of mercury atoms show a very strong intermixing of singlet and triplet character for the two levels with $J = 1$.

The practical importance of this intermixing of S is that transitions are allowed only between levels having the same S. However, the "spin-forbidden" transitions have some intensity, when the values of S are mixed, and may become indistinguishable from the spin-allowed transitions, when the intermixing is prominent. The development of "intermediate coupling," i.e., deviations from the Russell–Saunders approximation, is quantitatively expressed by the Landé parameter ζ_{nl}. In a strong-sense theory, the most important contribution to this parameter arises in the small part of the radial function which is very close to the nucleus (since it is a function of the gradient dU/dr of the central field U) and it is assumed by many authors that ζ_{nl} gives a reliable measure of $\langle r^{-3} \rangle$. However, this is less certain than the relation between F^k and $\langle r^{-1} \rangle$.

II. EVOLUTION OF THE LIGAND FIELD THEORY

A. Bethe's Results

Bethe[13] discussed in 1929 the idea that the neighbor atoms and molecules (now called ligands) have an influence on a transition group ion, which, to a first approximation, can be compared with an external electrostatic field of lower symmetry than the spherical, shifting the energy levels of the central ion and splitting several of them into more levels, due to the removal of the $(2l + 1)$-fold orbital degeneracy in spherical symmetry. Bethe intended at first to apply his theory to crystals containing lanthanide ions and hence called it crystal field theory.

The group-theoretical treatment of the Russell–Saunders approximation in nonspherical symmetry substitutes a quantum number Γ_n (and thus the new terms are characterized by S and Γ_n and written ${}^{2S+1}\Gamma_n$) for L and in the same way γ_n for l of the orbitals. The number of possible Γ_n depends on the symmetry, as discussed above, and, especially, the presence of sets of degenerate orbitals, i.e., Γ_n having the degeneracy number e above 1, is intimately connected with some elements of high symmetry (e.g., the equivalence of the three Cartesian coordinates x, y, and z in octahedral symmetry O_h).

In the case of O_h, the possible values of Γ_n are:

$$\begin{array}{rccccc} & \Gamma_1 & \Gamma_2 & \Gamma_3 & \Gamma_4 & \Gamma_5 \\ e = & 1 & 1 & 2 & 3 & 3 \\ \text{Mulliken:} & A_1 & A_2 & E & T_1 & T_2 \end{array} \tag{8}$$

As at several other points in the ligand field theory, synonymous nomenclatures have been developed, and we also indicate Mulliken's proposal, more directly connected with e, in Eq. (8). In octahedral symmetry O_h, the values of Γ_n are connected with even or odd parity, often denoted by g (for *gerade*) and u (for *ungerade*). This is also the case with atomic spectroscopy, where the values of L and J may be connected with either even or odd parity, while the parity of the orbitals l is even for l even and odd for l odd.

In tetrahedral symmetry without a center of inversion (T_d), the parity does not exist, but the five values of Γ_n are those from Eq. (8). In the lower, tetragonal symmetry D_{4h} (as mentioned above), the values are

$$\begin{array}{rccccc} & \Gamma_{t1} & \Gamma_{t2} & \Gamma_{t3} & \Gamma_{t4} & \Gamma_{t5} \\ e = & 1 & 1 & 1 & 1 & 2 \\ \text{Mulliken:} & A_1 & A_2 & B_1 & B_2 & E \end{array} \tag{9}$$

with lower degeneracy numbers e, we have added t in the subscript for distinction from the octahedral and tetrahedral Γ_n.

The terms with a given value of L in spherical symmetry correspond always to definite sets of values of Γ_n in the lower symmetries, and Bethe[13] calculated them in a large number of cases. Thus, for O_h:

$$\begin{array}{rcl} L = 0 & S & \Gamma_1 \\ 1 & P & \Gamma_4 \\ 2 & D & \Gamma_3 + \Gamma_5 \\ 3 & F & \Gamma_2 + \Gamma_4 + \Gamma_5 \\ 4 & G & \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5 \\ 5 & H & \Gamma_3 + 2\Gamma_4 + \Gamma_5 \end{array} \tag{10}$$

In the case of tetrahedral symmetry T_d, the numbers Γ_4 and Γ_5 are to be interchanged for odd parity of L, as is also the case for Γ_1 and Γ_2 of odd parity.

The tetragonal symmetry D_{4h} can be considered as a degradation of O_h, changing the behavior of one of the Cartesian axes from that of the two others, which remain equivalent. The values of Γ_{th} for a given L can be found from (10) with use of the correspondence

$$\begin{array}{rccccc} O_h: & \Gamma_1 & \Gamma_2 & \Gamma_3 & \Gamma_4 & \Gamma_5 \\ D_{4h}: & \Gamma_{t1} & \Gamma_{t3} & \Gamma_{t1} + \Gamma_{t3} & \Gamma_{t2} + \Gamma_{t5} & \Gamma_{t4} + \Gamma_{t5} \end{array} \tag{11}$$

Equations 8–11 can be immediately applied also to the γ_n of the orbitals, corresponding to a given l. For instance, the d shell of the central ion divides into two subshells, γ_3 consisting of two orbitals with the same energy, and γ_5 consisting of three orbitals with the same energy. We denote the energy difference between these two subshells by Δ, but many authors have used other symbols, such as $10Dq$ or $(E_1 - E_2)$.

If we want to predict all the terms (S,Γ_n) from a given number q of electrons in a partly filled d shell, we may either consider all the possible L,S terms in spherical symmetry and enumerate their octahedral levels according to Eq. (10), or we may consider the subshell configurations $\gamma_5^a\gamma_3^b$ with an integral number $0 \leqslant a \leqslant 6$ and $0 \leqslant b \leqslant 4$ of electrons in each of the two subshells. The latter process is a little complicated in the case of a partly filled subshell, in close analogy with the formation of L,S terms in spherical symmetry [cf. Eq. (5)]. However, it can be proved[111] that it is only necessary to know the following results

$$\begin{array}{llll}
\gamma_5^0 & {}^1\Gamma_1 & \gamma_3^0 & {}^1\Gamma_1 \\
\gamma_5^1 & {}^2\Gamma_5 & \gamma_3^1 & {}^2\Gamma_3 \\
\gamma_5^2 & {}^3\Gamma_4 + {}^1\Gamma_5 + {}^1\Gamma_3 + {}^1\Gamma_1 & \gamma_3^2 & {}^3\Gamma_2 + {}^1\Gamma_3 + {}^1\Gamma_1 \\
\gamma_5^3 & {}^4\Gamma_2 + {}^2\Gamma_3 + {}^2\Gamma_4 + {}^2\Gamma_5 & &
\end{array} \tag{12}$$

in addition to the multiplication tables for Γ_n given by Bethe[13] and reproduced for O_h in Table I. Pauli's hole-equivalency theorem that l^q and $l^{(4l+2-q)}$ in spherical symmetry present the same sets of L,S terms can be extended to subshell configurations, $\gamma_5^a\gamma_3^b$ presenting the same sets of ${}^{2S+1}\Gamma_n$ as $\gamma_5^a\gamma_3^{4-b}$, $\gamma_5^{6-a}\gamma_3^b$, or $\gamma_5^{6-a}\gamma_3^{4-b}$. If the "parent terms" of each of the subshells γ_5^a and γ_3^b are known, the terms of $\gamma_5^a\gamma_3^b$ can easily be found, since they represent all combinations possible of Γ_n from the multiplication table, combined with the values of S found as for spherical symmetry, i.e., $S = S_1 + S_2, S_1 + S_2 - 1, \cdot \cdot \cdot, |S_1 - S_2|$, where S_1 and S_2 are the values of S in the two parent terms. For instance, the terms of

$$\gamma_5\gamma_3 \quad \text{or} \quad \gamma_5^5\gamma_3 \quad \text{or} \quad \gamma_5^5\gamma_3^3 \qquad {}^3\Gamma_4 + {}^3\Gamma_5 + {}^1\Gamma_4 + {}^1\Gamma_5 \tag{13}$$

follow from the fact that the parent terms are ${}^2\Gamma_5$ and ${}^2\Gamma_3$, having the product $\Gamma_4 + \Gamma_5$ (Table I) and the possible values of $S = 1$ and 0.

TABLE I. Multiplication of Γ_n (single group) and Γ_J (double group) in Octahedral (O_h) and Tetrahedral (T_d) Symmetry. The Commutative Law $\Gamma_a \times \Gamma_b = \Gamma_b \times \Gamma_a$ Holds

Part a. $\Gamma_n \times \Gamma_n$	Part b. $\Gamma_n \times \Gamma_J$
$\Gamma_1 \times \Gamma_n = \Gamma_n$	$\Gamma_1 \times \Gamma_6 = \Gamma_2 \times \Gamma_7 = \Gamma_6$
$\Gamma_2 \times \Gamma_2 = \Gamma_1$	$\Gamma_2 \times \Gamma_6 = \Gamma_1 \times \Gamma_7 = \Gamma_7$
$\Gamma_2 \times \Gamma_3 = \Gamma_3$	$\Gamma_3 \times \Gamma_6 = \Gamma_3 \times \Gamma_7 = \Gamma_8$
$\Gamma_2 \times \Gamma_4 = \Gamma_5$	$\Gamma_3 \times \Gamma_8 = \Gamma_6 + \Gamma_7 + \Gamma_8$
$\Gamma_2 \times \Gamma_5 = \Gamma_4$	$\Gamma_4 \times \Gamma_6 = \Gamma_5 \times \Gamma_7 = \Gamma_6 + \Gamma_8$
$\Gamma_3 \times \Gamma_3 = \Gamma_1 + \Gamma_2 + \Gamma_3$	$\Gamma_5 \times \Gamma_6 = \Gamma_4 \times \Gamma_7 = \Gamma_7 + \Gamma_8$
$\Gamma_3 \times \Gamma_4 = \Gamma_4 + \Gamma_5$	$\Gamma_4 \times \Gamma_8 = \Gamma_5 \times \Gamma_8 = \Gamma_6 + \Gamma_7 + 2\Gamma_8$
$\Gamma_3 \times \Gamma_5 = \Gamma_4 + \Gamma_5$	
$\Gamma_4 \times \Gamma_4 = \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$	Part c. $\Gamma_J \times \Gamma_J$
$\Gamma_4 \times \Gamma_5 = \Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5$	$\Gamma_6 \times \Gamma_6 = \Gamma_7 \times \Gamma_7 = \Gamma_1 + \Gamma_4$
$\Gamma_5 \times \Gamma_5 = \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$	$\Gamma_6 \times \Gamma_7 = \Gamma_2 + \Gamma_5$
	$\Gamma_6 \times \Gamma_8 = \Gamma_7 \times \Gamma_8 = \Gamma_3 + \Gamma_4 + \Gamma_5$
	$\Gamma_8 \times \Gamma_8 = \Gamma_1 + \Gamma_2 + \Gamma_3 + 2\Gamma_4 + 2\Gamma_5$

Much has been written describing the differences in the nature of the "weak-field" approximation, considering the octahedral terms ${}^{2S+1}\Gamma_n$ as produced by the L,S terms of spherical symmetry, and the "strong-field" approximation, considering the octahedral terms as belonging to the subshell configurations $\gamma_5^a\gamma_3^b$. It is not possible here to outline the theory of secular determinants and the perturbation theory[37,54,126,238], but it may be noted that not only (of course) is the number of terms of each symmetry type Γ_n,S the same in the two descriptions but so also is their energy, when the calculation is completed in each of the two descriptions. However, the didactical difficulty is the following: only if only one term has a given combination of S and Γ_n, is its energy a simple linear combination $k_1\Delta + k_2B + k_3C$ of the orbital energy difference Δ and the parameters of interelectronic repulsion B and C (Eq. 6). If two terms belong to the same symmetry type, their energy is a square-root expression in Δ, B, and C, forming the two parts of a hyperbola in a diagram of energy as a function of Δ with fixed values of B and C. If three or more terms belong to the same symmetry type, the corresponding behavior of the eigenvalues is fairly complicated. Now, the diagonal elements of the weak-field determinants are the asymptotic straight lines approximating these curves for $\Delta \rightarrow 0$. The part $k_2B + k_3C$ of the weak-field diagonal element corresponds to the interelectronic repulsion energy of a given L,S-term, while the part $k_1\Delta$ may contain a decimal fraction k_1.

The nondiagonal elements of weak-field determinants are multiples of Δ. On the other hand, the diagonal elements of the strong-field determinants are the asymptotes for $\Delta \rightarrow \infty$. If the "baricenter" rule, valid for the electrostatic model, is maintained, the number k_1 in $k_1\Delta$ of the strong-field diagonal element is simply related to the subshell configuration $\gamma_5^a\gamma_3^b$ by

$$k_1 = -0.4a + 0.6b \tag{14}$$

while $k_2B + k_3C$ does not necessarily correspond to one L,S term, but may be a linear combination of several terms.

The latter concept was introduced by Mulliken as a "valence state." The nondiagonal elements of strong-field determinants are linear combinations of B and C. The "diagonal sum rule" states that in two equivalent determinants (such as the weak-field and strong-field determinants for d^q), the sum of the coefficients of each of the variables (Δ, B, and C) is invariant. Another rule states that the sum of the squares of all coefficients (the nondiagonal elements E_{mn} and E_{nm} both taken) to a given variable is also invariant.

The intermediate coupling, i.e., deviations from the Russell–Saunders approximation, was also treated by Bethe.[13] We may here distinguish between systems with an even or an odd number of electrons. In spherical symmetry, J and S are integers, as is L, for an even number, while J and S are half integers 1/2, 3/2, 5/2, · · · for odd electron numbers. The same intrinsic difference occurs in lower symmetries, e.g., for O_h the new quantum number Γ_J has the same value for a given J as the function of L in Eq. (10). On the other hand, three values of Γ_J, viz., Γ_6 ($e = 2$), Γ_7 ($e = 2$), and Γ_8 ($e = 4$), occur for octahedral systems with an odd number of electrons. Griffith[77] proposes the names E', E'', and U'.

It is seen from the values of the degeneracy number e that Kramers' theorem that an even number of independent wave functions always participates in the energy level of a system with an odd number of electrons is valid. Kramers' degeneracy can only be removed by external magnetic, not electrostatic, fields (Zeeman effect).

The number of independent states in a term is $(2S + 1)(2L + 1)$ in spherical and $(2S + 1)e$ in lower symmetries, e being the orbital degeneracy. The number of independent states in an individual level is $2J + 1$ in spherical symmetry. The values of Γ_J for a given ${}^{2S+1}\Gamma_n$ is found from the multiplication table, assigning the values of Eq. (10) for integral S values (Γ_1 for singlets, Γ_4 for triplets, $\cdot\cdot\cdot$) and other values for half integers (Γ_6 for $S = 1/2$, Γ_8 for $S = 3/2$, $\cdot\cdot\cdot$) and multiplying these Γ by Γ_n.

This form of the ligand field theory, as outlined above, contains one restrictive assumption: that the orbitals and energy levels of the transition-group compound behave exactly as if the partly filled shell had a well-defined l from spherical symmetry. However, we must realize that Eq. (10) is not at all a biunial relation. It is true that a given value of l, for example 2, corresponds to quite definite values of γ_n in the lower symmetry, such as γ_3 and γ_5; but it is not necessarily true that a given orbital γ_n in the compound corresponds to a definite value of l. Actually, Mulliken[188] and Hund[102] emphasized as early as 1930 that a much more comprehensive and realistic description of all molecules could be obtained by the molecular orbital theory.

In the same way as the central field of spherical symmetry determines the one-electron wave functions of the n,l shells, Eq. (1), we can imagine a molecular "core field" of appropriate, lower symmetry generate molecular orbitals (in the following abbreviated M.O.) with definite γ_n. The salient point is our hope that M.O. configurations $\gamma_n^a \gamma_m^b \gamma_k^c \cdot\cdot\cdot$ may be good approximations or at least be able to classify the observed energy levels S,Γ_n in the same way as the n,l-electron configurations in atomic spectroscopy.[186]

B. Comparison with Diatomic Molecules

Following the identification of a very great number of energy levels of gaseous atoms and ions from Rydberg's time to about 1930, the diatomic molecules in gaseous state were the next entities to attract the spectroscopists. There are many reasons: there exists only one normal mode of vibration, and, consequently, the energy differences due to vibrational and rotational motion (being much smaller in most cases than the "electronic" energy differences) could be theoretically interpreted and used for indicating internuclear distances and force constants; and a single potential curve as function of *the* internuclear distance exists for each "electronic" energy level. Actually, the ground states and the lower excited levels happened to agree extremely well with a M.O. classification.

The reader is here asked to excuse the further multiplication of symbols. The quantum numbers Γ_n, Γ_J, and γ_n are called Λ, Ω, and λ, respectively, in the two linear symmetries $D_{\infty h}$ (with a center of inversion) and $C_{\infty v}$ (without). Further, in analogy with Eq. (2), special names have been given to the smaller values of Λ and λ:

$$\begin{array}{llllll} \lambda = 0 & \sigma & (e = 1) & \quad \Lambda = 0 & \Sigma \\ \lambda = 1 & \pi & (e = 2) & \quad \Lambda = 1 & \Pi \\ \lambda = 2 & \delta & (e = 2) & \quad \Lambda = 2 & \Delta \\ \lambda = 3 & \phi & (e = 2) & \quad \Lambda = 3 & \Phi \end{array} \tag{15}$$

To make the complication perfect, a distinction is finally possible for $\Lambda = 0$ (but not for $\lambda = 0$) between Σ^+ and Σ^- according to the behaviour of the more-electron wave function on reflection in a plane containing the linear axis. However, the two linear symmetries have good reasons for demanding a special treatment.

Thus, the number of possible λ is infinite, being all non-negative integers, while the number of possible γ_n is finite, and rather low, in all the other symmetries we consider here. The set of orbitals, corresponding to a definite value of l, is simply $\lambda = 0, 1, 2, \cdot\cdot\cdot, l$.

In homonuclear, diatomic molecules, a center of inversion exists, and, hence, the λ orbitals are further characterized by parity (g and u for even and odd). A study of H_2, Li_2, C_2, N_2, O_2, F_2, Na_2, $\cdot\cdot\cdot$ demonstrated clearly that the order of energy of these orbitals are

$$\begin{array}{ccccccccccc} 1\sigma_g & 1\sigma_u & \ll 2\sigma_g & 2\sigma_u & 1\pi_u & 3\sigma_g & < 1\pi_g & < 3\sigma_u & \ll 4\sigma_g & \cdots \\ 1s & 1s & 2s & 2s & 2p & 2p & 2p & 2p & 3s & \end{array} \tag{16}$$

the inequality signs indicating especially conspicuous energy differences. The n,l symbols below do not refer to a (nonexistent) central atom, but to the fact that in homonuclear molecules, it seems a fairly good approximation to the one-electron wave functions to write them as linear combinations of the atomic orbitals of the two atoms. If we take the linear axis (containing the two nuclei) as the z axis, we may denote the atomic orbitals s, x, y, z [cf. Eq. (3)] by subscripts 1 and 2 for the two atoms, and neglecting normalization constants write the orbitals of Eq. (16) for the $2s$ and $2p$ shell:

$$\begin{array}{ll}
\text{bonding } 2\sigma_{\mathrm{g}}: & \text{bonding } 3\sigma_{\mathrm{g}}: \\
\quad s_1 + s_2 & \quad z_1 - z_2 \\
\text{anti-bonding } 2\sigma_{\mathrm{u}}: & \text{anti-bonding } 1\pi_{\mathrm{g}}: \\
\quad s_1 - s_2 & \quad x_1 - x_2 \text{ and } y_1 - y_2 \\
\text{bonding } 1\pi_{\mathrm{u}}: & \text{anti-bonding } 3\sigma_{\mathrm{u}} \\
\quad x_1 + x_2 \text{ and } y_1 + y_2 & \quad z_1 + z_2
\end{array} \tag{17}$$

Since the electron density of the orbital $(a_1 + a_2)$ is proportional to $(a_1 + a_2)^2$, it is seen that a supplementary electron density $2a_1a_2$ resides in the "overlap region" between the two atoms. Actually, the quantities s_1s_2, x_1x_2, and y_1y_2 are positive between the two atoms, while z_1z_2 is negative, due to the direction of the z axis. Hence, the orbitals $2\sigma_{\mathrm{g}}$, $1\pi_{\mathrm{u}}$, $3\sigma_{\mathrm{g}}$ are marked "bonding" in Eq. (17) because they concentrate a part of their electron density in the region between the two atoms, while the orbitals $2\sigma_{\mathrm{u}}$, $1\pi_{\mathrm{g}}$, and $3\sigma_{\mathrm{u}}$ are marked "anti-bonding" because they have decreased density in the bond region and especially because they have a node plane where the density is zero. The distinction between bonding and antibonding M.O. is to some extent an artificial simplification, since we cannot expect the atomic orbitals in Eq. (17) to be the only components of the wave function. The approximation L.C.A.O. (linear combination of atomic orbitals) is rather qualitative when it takes only one (or a few) orbitals into account from each atom. On the other hand, the more mathematical expression of L.C.A.O. as an expansion of the M.O. as a linear combination among an infinite set of atomic orbitals on each atom involves many difficulties, since the sets are overcomplete.

Actually, one of the greatest early victories of the M.O. theory was the explanation of the paramagnetism of the oxygen molecule, which cannot be understood in the usual electron-pair bond description of chemical bonding. Filling 16 electrons of O_2 into the orbitals of Eq. (16) gives $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 1\pi_g^2$ as the lowest configuration. The two equivalent orbitals $1\pi_g$ constitute a partly filled shell and hence have terms of different symmetry types, viz., $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$, belonging to the same configuration and separated by parameters of interelectronic repulsion. The internuclear distance at the minimum of the potential curve is a sensitive function of the M.O. configuration[167,184] increasing with the number of occupied anti-bonding M.O., but is very nearly the same for the triplet ground state and the two low singlets (the transitions produce some of the Terrestrian–Fraunhofer lines in the sun spectrum, filtered by the atmospheric oxygen). The nitrogen molecule, having two electrons less than O_2, has a typical closed-shell M.O. configuration with the excited states at very high energy, i.e., in the far ultraviolet. On the other hand, the carbon molecule C_2 which can be observed in some flames has several terms at low energy, since the orbitals $1\pi_u$ and $3\sigma_g$ have nearly the same energy.

Turning to transition-group complexes, Van Vleck[249] remarked in 1935 that the M.O. theory and the ligand field theory agree on the qualitative results of the energy level distribution, e.g., in octahedral complexes of the form MX_6 or square-planar tetragonal MX_4. It may be useful first to consider the atomic orbitals of the central atom M with the low l values 0, 1, and 2. The angular functions from Eq. (4) illustrate the group-theoretical results given in Eqs. (10) and (11).

It is obvious that the constant A_l of the s electron does not change sign or value by any rotation or other group-theoretical operation on the molecule MX_n and hence it has the totally symmetric type γ_1 in all symmetries. The three A_l of the p electron, proportional to x, y, and z, are equivalent in an octahedral complex MX_6 where the names of the three Cartesian axes can be interchanged without varying the physical situation, and they constitute the odd γ_4 with $e = 3$. On the other hand, in a complex with the symmetry D_{4h}, such as square-planar MX_4 or even MX_6 with the ligands on one axis closer to M or more distant from M than the other four ligands, or MX_4Y_2 with the two Y on one axis, the three p orbitals will no longer be equivalent. If the tetragonal axis is called z, the two orbitals x and y are still equivalent, constituting the odd γ_{t5} with $e = 2$, while z now is odd γ_{t2}.

Among the five d orbitals, it is also evident that yz, xz, and xy are equivalent in octahedral symmetry, forming even γ_5. It is less evident that $(x^2 - y^2)$ and $(2z^2 - x^2 - y^2)$ are equivalent in MX_6, but it can be proved that any perturbation which is invariant for a cyclic permutation of x, y, and z perturbs the two (even γ_3) orbitals to the same extent. The behavior of the five d orbitals in square-planar MX_4 and linear MX_2 is:

$$\begin{array}{lcccc} & xz,yz & xy & (2z^2 - x^2 - y^2) & (x^2 - y^2) \\ D_{4h} & \gamma_{t5} & \gamma_{t4} & \gamma_{t1} & \gamma_{t3} \\ D_{\infty h} & \pi & \delta & \sigma & \delta \end{array} \tag{18}$$

The electrostatic model of the ligand field assumes that the energy difference Δ between γ_5 and γ_3 is caused by the fact that the ligands have negative charges or are polarized with the negative end toward the central ion, and γ_3 is concentrated in the six directions toward the ligands, while the three γ_5 orbitals are mainly concentrated between the ligands. Actually, the squared angular functions from Eq. (4) of the two γ_3 and three γ_5 are:

$$\begin{array}{rl} 2(\gamma_3)^2: & (x^4 + y^4 + z^4 - x^2z^2 - y^2z^2 - x^2y^2)/r^4 \\ 3(\gamma_5)^2: & 3(x^2y^2 + x^2z^2 + y^2z^2)/r^4 \\ 2(\gamma_3)^2 + 3(\gamma_5)^2: & (x^2 + y^2 + z^2)^2/r^4 = 1 \end{array} \tag{19}$$

It is seen that the electron densities of the three γ_5, taken together, are concentrated in the direction of the eight corners of a cube, inscribed in the regular octahedron, and that the sum of electron densities of a closed shell $\gamma_5^6\gamma_3^4$ (or the level $^6\Gamma_1$of the half-filled shell $\gamma_5^3\gamma_3^2$) is spherically symmetric. It has been customary to separate the ligand field V into components

$$V = V_0 + V_{\text{oct}} + V_{\text{tetr}} + \cdots \tag{20}$$

where V_0 is spherical symmetric, without angular dependence, and V_{oct} is the specifically octahedral part, which is dependent on x, y, z in such a way that the function is independent of interchange of the three coordinates. V_{tetr} is a further contribution to the ligand field which can be incorporated in neither V_0 nor V_{oct}, but is invariant for exchange of x and y, and so on. With the distribution equation (20), only V_0 changes the energy of a closed shell such as $\gamma_5^6\gamma_3^4$, while the energy decrease of γ_5 and increase of γ_3 under the influence of V_{oct} compensate each other exactly, causing the baricenter of a configuration, i.e., its average energy when each level is weighted with its degeneracy number, to be constant under the influence of all the components of V with lower symmetry than V_0.

After this survey of the fate of the most important orbitals of the central atom in the core-field of the complex, we may next discuss the orbitals of the ligands. In an octahedral complex, the core-field acting on a ligand has the symmetry C_{4v}, which can reasonably well be approximated by $C_{\infty v}$, the linear symmetry without center of inversion. Consequently, λ of Eq. (15) is a fairly good quantum number for the orbitals of the ligands. We have different types of ligand atoms, also those included in other molecules. The ion H^- and many molecules with one "lone pair" such as ammonia and other amines $R_1R_2R_3N$ have a σ orbital as the loosest bound M.O. in the core-field of the central ion. The halogen ions F^-, Cl^-, Br^-, I^-, and ions such as O^{2-} and S^{2-} have closed-shell structures, containing six p electrons as the most loosely bound electrons. As we saw above, this filled p shell divides into two π orbitals with the same energy and one σ orbital, directed toward the positive central ion and hence of lower energy. Finally, molecules with two lone pairs such as H_2O or $R_1R_2N^-$ contribute in a certain sense only one of the two π orbitals and one σ orbital.

Van Vleck[249] indicated the γ_n and parity of the six σ orbitals in MX_6 and the four σ orbitals in square-planar MX_4, while Kimball[147] later indicated similar results for the π orbitals in complexes. Tables II and III give the appropriate linear combinations of the ligands' orbitals for each symmetry type, neglecting normalization constants.

Knowing the γ_n and parity of the orbitals of both the ligands and the central atom, we may then argue qualitatively from the L.C.A.O. approximation the shapes and the order of energy of the M.O. formed. We note here the nature of the concept of "inner shells in localized atomic orbitals" as distinct from "true delocalized molecular orbitals". If both the bonding and the antibonding M.O. of the type $a_1 + a_2$ and $a_1 - a_2$ of Eq. (17) are

TABLE II. Linear Combinations of Atomic Orbitals Which May Participate in M.O. Formation in Regularly Octahedral Complexes MX_6. A Cartesian (x,y,z) System is Used with the Central Atom M at (0,0,0) and the Ligands X Numbered: 1:(1,0,0); 2:(−1,0,0); 3:(0,1,0); 4:(0,−1,0); 5:(0,0,1); and 6:(0,0,−1). The σ Orbitals are Characterized by Their Ligand Number as Subscript, while the π Orbitals are Assumed to be the p Orbitals x_q and y_q Belonging to the Ligand No. q and Having the Appropriate Direction in the Cartesian Coordinate System. Normalization Constants are Not Indicated

	Ligand orbitals	Central atom orbitals
even γ_1	$\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6$	$s(1)$
even γ_3	$2\sigma_5 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4$	$2z^2 - x^2 - y^2$
	$\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4$	$x^2 - y^2$
even γ_4	$z_3 - z_4 - y_5 + y_6$	
	$z_1 - z_2 - x_5 + x_6$	
	$y_1 - y_2 - x_3 + x_4$	
odd γ_4	$\sigma_1 - \sigma_2$	$p(x)$
	$\sigma_3 - \sigma_4$	$p(y)$
	$\sigma_5 - \sigma_6$	$p(z)$
	$x_3 + x_4 + x_5 + x_6$	
	$y_1 + y_2 + y_5 + y_6$	
	$z_1 + z_2 + z_3 + z_4$	
even γ_5	$z_3 - z_4 + y_5 - y_6$	yz
	$z_1 - z_2 + x_5 - x_6$	xz
	$y_1 - y_2 + x_3 - x_4$	xy
odd γ_5	$x_3 + x_4 - x_5 - x_6$	
	$y_1 + y_2 - y_5 - y_6$	
	$z_1 + z_2 - z_3 - z_4$	

filled, the total electron density is very close to that of the separate orbitals a_1 and a_2. Hence, the formation of M.O. from distant, nonoverlapping atomic orbitals does not have any consequences for the actual electron densities in the inner shells of the various atoms. This mathematical transformation is only necessary for the formation of well defined γ_n, which is of importance for the possible excitation or ionization processes in the closed-shell systems. Since we are mainly interested in the most loosely

TABLE III. Linear Combinations of Atomic Orbitals Which May Participate in M.O. Formation[11a] in Square-Planar Complexes MX_4. The Notation is the Same as in Table II, Except That the Ligands on the z Axis Have Been Removed

	Ligand orbitals	Central atom orbitals
even γ_{t1}	$\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4$	$s(1)$ $2z^2 - x^2 - y^2$
even γ_{t2}	$y_1 - y_2 - x_3 + x_4$	—
odd γ_{t2}	$z_1 + z_2 + z_3 + z_4$	$p(z)$
even γ_{t3}	$\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4$	$x^2 - y^2$
even γ_{t4}	$y_1 - y_2 + x_3 - x_4$	xy
odd γ_{t4}	$z_1 + z_2 - z_3 - z_4$	—
even γ_{t5}	$z_1 - z_2$	xz
	$z_3 - z_4$	yz
odd γ_{t5}	$\sigma_1 - \sigma_2$	$p(x)$
	$\sigma_3 - \sigma_4$	$p(y)$
	$x_3 + x_4$	
	$y_1 + y_2$	

bound M.O. of highest energy, we neglect in the following the inner shells in our enumeration of M.O. formed, but we realize that it is not due to a difference in species of the inner shells and the delocalized orbitals.

Many arguments to be presented later show that the partly filled shell of the three transition groups in complexes has a higher energy than the orbitals of the ligands. Hence, the two equivalent orbitals even γ_3 of the partly filled shell form the antibonding component of a linear combination, whose bonding component is mainly concentrated in the ligands, being the σ orbitals even γ_3 of Table II. In other words, one of the effects of covalent bonding in complexes will be that the two sets of M.O. having the symmetry type even γ_3 are delocalized on both the central atom and the ligands. The bonding set of low energy has a density maximum in the bond region between the ligands and the central atom, while the antibonding set has a density minimum there. The corresponding increase of energy of the latter set contributes to increasing Δ, since the other part of the partly filled shell, even γ_5, is not affected by the σ bonding. On the other hand, even γ_5

may form the antibonding component with the three (of the twelve) π orbitals even γ_5 of Table II. This π bonding, increasing the energy of the antibonding component, decreases Δ.

If the influence of the central ion on each ligand could be exactly identified with the action of a field with symmetry $C_{\infty v}$, the 12 σ electrons of an octahedral hexahalide complex would have the same energy, and the 24 π electrons would have an identical, higher energy. There are two reasons for the splitting of energy between the three sets of σ orbitals and four sets of π electrons in Table II, viz., the interaction with the n,l orbitals of the central atom and the mutual interaction between the 6 halogen atoms (destroying the validity of λ). In general, the influence of the central ion shells is expected to be largest for the smallest values of l. Hence, the nonbonding sets even γ_4 and odd γ_5 are expected to have highest energy among the π electrons, the other being stabilized by the formation of bonding combinations. The halogen–halogen interactions give the same order of stability, as mentioned by McClure[179] arguing from the number of node planes between the orbitals in Table II. Actually, the number of node planes is identical with the lowest value of l of the central ion, with which the ligands' orbitals with given γ_n are able to interact. It is possible to find this minimum value of l (given in parentheses in (21)) from an extension of (10):

$$\begin{array}{llllll} \text{even} & \gamma_1(0) & \gamma_2(6) & \gamma_3(2) & \gamma_4(4) & \gamma_5(2) \\ \text{odd} & \gamma_1(9) & \gamma_2(3) & \gamma_3(5) & \gamma_4(1) & \gamma_5(3) \end{array} \qquad (21)$$

Among the linear combinations of orbitals from the ligands of an octahedral complex, the two sets odd γ_4 are unique in allowing a mixture of σ and π character. This will be shown later to be of great importance for the absorption spectra of certain hexahalide complexes.

The essentially different points of view of the electrostatic model of the ligand field and the more general M.O. theory are connected with an old distinction in chemistry between electrostatic and covalent bonding. The concept "valency" developed mainly in inorganic chemistry to "oxidation number", positive or negative, while organic chemists developed "coordination number", the positive number of atoms directly attached to a given atom. When double and triple bonds were introduced, the "bond number" was assumed to be constant, such as 4 for carbon, being the sum of the "bond orders" of the individual bonds. Later, fractional bond orders were assumed in some cases, as 1.5 in benzene and in the carboxylate group.

Lewis maintained that the covalent bond with bond order 1 is connected with an electron pair, shared between the two atoms. This bond could be more or less polar if the two atoms are different, the electron pair being asymmetrically concentrated near one of the two atoms. On the other hand, many compounds were assumed to be constituted by ions having electric charges equal to the oxidation numbers. Kossel remarked on the very good agreement between the electrostatic Madelung energy and the heat of formation of many crystalline salts from the ions, e.g., if it was assumed that sodium chloride consists of Na^+ and Cl^- and barium oxide of Ba^{2+} and O^{2-}. It was, on the other hand, evident that compounds such as CCl_4 and CO_2 could not be assumed to consist of fully charged ions C^{4+}, Cl^-, and O^{2-}, though the oxidation numbers are defined as $+4$, -1, and -2.

Anhydrous halides seem to fall into two classes: salts melting at high temperatures and then having electric conductivity, and gases or liquids freezing at low temperatures and being electric insulators. It was believed for many years that the former class had electrostatic and the second class covalent bonding. This concept was extended to transition-group complexes, using the German words "Anlagerung" and "Durchdringung" complexes. However, we shall see that this distinction is futile and that the M.O. theory allows a unified description of all complexes.

We have not yet defined a "complex." Chemists mainly use the word for one or several fairly heavy metal atoms having quite strong chemical bonds to a number of surrounding ligands. However, logically, there does not seem to be a sharp distinction possible for molecules in general. $Be(H_2O)_4^{2+}$, BF_4^-, SO_4^{2-}, and ICl_4^- are not essentially different from other complexes. It cannot be a question of either ionic charge or neutrality. The "inner salts" such as the neutral acetylacetonates have been considered as complexes for many years, and there is no serious reason now to distinguish RuO_4 and ReF_6 from RuO_4^{2-} and ReF_6^{2-}. Hence, we continue to use the word "complex" in a fairly loose manner, signifying polyatomic molecules or ions, containing atoms of the metallic elements.

C. Energy Levels of the 3*d*, 4*d*, 5*d* Groups

Although in principle all the ideas outlined above were developed before 1935, they did not meet many applications before 1951. This is a most surprising fact, partly explained by the objection to mathematics, especially group theory, among chemists, and partly explained by the enormous success of the valency-bond and hybridization theory, widely publicized by Linus Pauling. The latter theory, though very ingenious, slowed down the progress of the knowledge of the energy levels of the transition-group complexes. However, it must be admitted that several of the points of view mentioned above were not clearly stated in the literature before quite recently.

Actually, the electrostatic model of the ligand field was used since 1930 by Van Vleck and many others for explaining subtle effects on the paramagnetic behavior of 3*d* complexes. They are mainly connected with the fine structure of the lowest term, i.e., energy levels with a spreading below 1000 cm^{-1}, comparable to the Boltzmann energy per degree of freedom at room temperature (210 cm^{-1}), while the visible light quanta are distributed between 13,000 (red) and 25,000 (violet) cm^{-1}. Very many magnetochemical problems were investigated, but it was not even certain whether Δ of ordinary 3*d* complexes has the order of magnitude 1000 or 10,000 cm^{-1}. A few magnetochemical studies, such as that of nickel(II) by Becquerel,[11] cobalt(II) by Abragam and Pryce,[1] and copper(II) by Polder,[210b] mention comparison with optical spectra, all concerning the hexaaquo ions. (We write the oxidation numbers in parentheses with Roman numerals after the name or the chemical symbol of the element, reserving ionic charges Ni^{2+} or U^{6+} for gaseous ions.)

However, the most elaborate attempt to identify the excited levels was made by Finkelstein and Van Vleck[55] in 1939. Small concentrations of chromium(III) in Al_2O_3 (corundum) constitute the red ruby with groups of very narrow absorption lines in the red at 14.400 and in the blue at 21.000 cm^{-1}. Finkelstein and Van Vleck calculated all the weak-field secular determinants for

d^3 in O_h and concluded that the line groups in the red are caused by transition from the ground state $^4\Gamma_2$ to the two coinciding excited terms $^2\Gamma_3$ and $^2\Gamma_4$, while the line group in the blue has $^2\Gamma_5$ as excited term. These transitions are very weak, being spin-forbidden. The energy levels involved all belong to the subshell configuration γ_5^3 [Eq. (12)].

They were disappointed that broad absorption bands of the ruby at 18.000 and 24.500 cm^{-1} masked the predicted position of the spin-allowed transitions to $^4\Gamma_5$ and $^4\Gamma_4$ (of the subshell configuration $\gamma_5^2\gamma_3$).

Many years later it was realized that the broad absorption bands are simply caused by the spin-allowed transitions. Orgel[198] explained the great difference in band-width expected from the Franck–Condon principle when the excited level belongs to another subshell configuration with changed internuclear distances for the minimum of the potential curve, compared to the single lines produced by internal transitions in a subshell configuration.

In 1951, Ilse and Hartmann[105] published a paper on the titanium(III) hexaaquo ion, having a broad absorption band at 20.300 cm^{-1}. (Actually, the band is double, with a shoulder at 17.400 cm^{-1} which must be interpreted as $Ti(H_2O)_6^{3+}$ deviating slightly from a regular octahedron.) Since gaseous Ti^{3+} has only one 3*d* electron outside the closed argon shells, Ilse and Hartmann maintained that the transition could be nothing else than from $^2\Gamma_5$ to $^2\Gamma_3$, assuming $\Delta = 20.300$ cm^{-1}. This was a very important argument; Kato, Deutschbein, and several other authors had previously suggested that the narrow and broad absorption bands observed of complexes containing several *d* electrons were simply transitions to excited *L*,*S* terms, having another position than in the gaseous ion. This explanation, which is now accepted for the 4*f* and 5*f* complexes, had always been somewhat doubtful for *d* complexes, since the ligands have so large an influence on the absorption spectra of a given central ion in the latter case. Hence, ^2D was clearly demonstrated to be split strongly in the titanium(III) complex. Ilse and Hartmann tried to obtain numerical agreement between the observed value of Δ and an electrostatic first-order perturbation calculation, assuming the external field produced by six point dipoles acting on a 3*d* electron, whose radial function is hydrogenic and has the effective charge according to Slater's rules. There is no doubt[118] that this numerical agreement is completely accidental; the hypothesis of an external ligand field will be criticized below, and we know from Hartree's calculation[91,256] that the radial functions are not at all hydrogenic, that the Slater charges do not agree with many other properties of the gaseous $3d$ ions, and that, worst of all, the radial functions of the gaseous ions overlap considerably with the ligands, provoking the formation of M.O.

Hartmann and Schläfer[83] in 1951 extended the discussion to the hexaaquo ions of vanadium(III), chromium(III), manganese(III), and iron(III). These authors applied the weak-field diagonal elements (see page 45) to the spin-allowed, broad bands, considering only the terms originating from the lowest L,S term of the gaseous ion. This assumption leads to erroneous identifications; the two broad bands of V(III) have ${}^3\Gamma_5$ and ${}^3\Gamma_4$ as excited levels [of $\gamma_5\gamma_3$, see Eq. (13)] and not ${}^3\Gamma_5$ and ${}^3\Gamma_2$ (as ^{3}F). The two broad bands of Cr(III) (we met above of the ruby) were correctly assigned to ${}^4\Gamma_5$ and ${}^4\Gamma_4$, but the distance calculated is much too large if the interaction with the other ${}^4\Gamma_4$ (of ^{4}P) is not taken into account. Qualitatively, it was explained why the d^4-system Mn(III) has only one spin-allowed transition (${}^5\Gamma_3$ to ${}^5\Gamma_5$) and why the d^5-system Fe(III) with the ground state ${}^6\Gamma_1$ has no spin-allowed transitions at all.

Orgel[195] published in 1952 a very condensed paper on ligand field theory, indicating, among many other results, the terms with maximum S of octahedral d^2 systems [i.e., vanadium(III) complexes] as function of Δ. This type of diagram, beginning with the corresponding gaseous ion at $\Delta = 0$, is now called an Orgel diagram. The 1952 paper was especially concerned with the heats of hydration of $3d$ ions. As already suggested by Penney[207] in 1940, the "ligand field stabilization" can be expressed by the negative values of k_1 in Eq. (14) for the ground states of many complexes, compared to a linear interpolation between the empty shell d^0, the half-filled shell d^5 (with $S = 5/2$), and the closed shell d^{10}, all having $k_1 = 0$. Thus, it explains the fact that complexes of iron(II), cobalt(II), and nickel(II) are more stable (have higher formation constants and higher heats of formation) than interpolated between manganese(II) and zinc(II). The stabilizations found in this way agree fairly well with the theoretical values of

(14), connected with the values of Δ derived from optical absorption spectra. Ligand field stabilizations have been further discussed by J. Bjerrum and the present author[17] and by George and McClure,[72] but there is no doubt that covalent bonding has a considerable influence on the bonding energies, sometimes causing deviations from (14), as discussed by Williams.[260] Nor, on the other hand, is there any doubt that the formation of subshell configurations $\gamma_5^a\gamma_3^b$ with $3b$ different from $2a$ ($2a = 3b$ is the case for filled shells and for half-filled shells with $S = 5/2$) is the main reason for the non-monotonic variation of many properties within the transition groups, such as the ionic radii (cf. Santen and Wieringen[218] and Hush[103]) increasing with the number b of σ antibonding electrons.

However, we shall here concentrate on spectroscopical evidence. During 1956 and 1957, it became clear that *no essential difference exists between the absorption spectra of the three transition groups.* Thus, Hartmann and Schmidt[88] measured $MoCl_6^{3-}$, showing two broad bands and, at lower wave numbers, two sets of narrow, spin-forbidden bands, showing the similarity between the usual Cr(III) ($3d^3$) and Mo(III) ($4d^3$) complexes. The present author found also the narrow, spin-forbidden bands[113] of $5d^3$ of the Re(IV) systems $ReCl_6^{2-}$ and $ReBr_6^{2-}$ but misinterpreted the excited levels.[123] Especially close analogies exist between the spectra of the diamagnetic d^6 systems, such as cobalt(III), rhodium(III), and iridium(III) complexes. The spectra of $3d^6$ [Co(III)] were measured by many authors, such as Tsuchida[235,247], Kiss,[149] Linhard and Weigel,[163–165] and Basolo.[10] The present author[115] measured the $4d^6$ complexes such as $RhBr_6^{3-}$, $RhCl_6^{3-}$, $Rh(H_2O)_6^{3+}$, $Rhox_3^{3-}$, $Rh(NH_3)_5I^{2+}$, $Rh(NH_3)_5Br^{2+}$, $Rh(NH_3)_5Cl^{2+}$, $Rh(NH_3)_5(H_2O)^{3+}$, $Rh(NH_3)_5(OH)^{2+}$, $Rh(NH_3)_6^{3+}$, and $Rhen_3^{3+}$, and $5d^6$ complexes such as $IrBr_6^{3-}$, $IrCl_6^{3-}$, and $Ir(NH_3)_5Cl^{2+}$. More recently, a series[124] of Rh(III) and Ir(III) complexes of pyridine, ammonia, oxalate and other anions, mainly prepared by M. Delépine, have been studied. Perros[208] found that the spectrum of PtF_6^{2-} resembles very closely that of $IrCl_6^{3-}$ with regard to the relative band positions and intensities. Generally, the d^6 systems exhibit one weak, but broad, spin-forbidden band, followed by two broad, stronger bands. The excited levels of these transitions are $^3\Gamma_4$, $^1\Gamma_4$, and $^1\Gamma_5$ of $\gamma_5^5\gamma_3$ (cf. (13) and Table VI), while the ground state is the only level, $^1\Gamma_1$, of the closed subshell γ_5^6. The intensity of the spin-forbidden bands increases with the principal quantum number n in such a way that the band maxima has 0.5% as high molar extinction coefficient ε as the spin-allowed bands in Co(III), while the ratio is 3% in Rh(III) and 12% in Ir(III) and Pt(IV). It is possible[117,126] to calculate the values of the effective non-diagonal elements of intermediate coupling (close to ζ_{nl}) from these intensity ratios, and the following values are found, in cm^{-1}:

$$\begin{array}{llllll} \mathrm{Co(III)} & 500 & \mathrm{Rh(III)} & 900 & \mathrm{Ir(III)} & 2000 \\ \mathrm{Co}^{3+} & 600 & \mathrm{Rh}^{3+} & 1400 & \mathrm{Ir}^{3+} & 4500 \end{array} \tag{22}$$

and compared to the (extrapolated) values of ζ_{nd} for the gaseous ions. Linhard and Weigel[166] found later that in complexes containing heavy ligand atoms, the spin-forbidden bands may become more intense. Thus, the apparent value of the non-diagonal element is 2000 cm^{-1} in $\mathrm{Co(NH_3)_5Br^{2+}}$ and 4000 cm^{-1} in $\mathrm{Co(NH_3)_5I^{2+}}$. Undoubtedly, this effect is connected with the fact that ζ_{np} is as high as 2457 cm^{-1} in gaseous Br and 5069 cm^{-1} in I.

In 1959, Moffitt, Goodman, Fred, and Weinstock[185] published the spectra of gaseous $\mathrm{ReF_6}$ ($5d$), $\mathrm{OsF_6}$ ($5d^2$), $\mathrm{IrF_6}$ ($5d^3$), and $\mathrm{PtF_6}$ ($5d^4$), and interpreted the narrow bands in the infrared and the red as the internal transitions in the subshell configuration γ_5^n, assuming strong effects of intermediate coupling (actually with $\zeta_{5d} = 3400$ cm^{-1} in all four molecules). The values extrapolated for the corresponding gaseous ions increase from 4000 cm^{-1} in Re^{6+} to 7500 cm^{-1} in Pt^{6+}, showing increasing importance of covalent bonding in the more oxidizing Pt(VI) compound. The present author[138] does not agree that the broad bands in the ultraviolet are caused by the "ligand field" transitions $\gamma_5^n \rightarrow \gamma_5^{n-1}\gamma_3$ in $\mathrm{OsF_6}$, $\mathrm{IrF_6}$, and $\mathrm{PtF_6}$, but argues that the wave numbers are close to those expected from electron transfer spectra, where an electron is excited from the filled sets of M.O. (mainly π electrons of the ligands) to the available holes in the γ_5 subshell.

At nearly the same time,[134] the present author discussed the internal γ_5^4 transitions in the Os(IV) complexes $\mathrm{OsCl_6^{2-}}$ and $\mathrm{OsBr_6^{2-}}$. These various pieces of evidence show clearly that there is no essential difference between the energy levels of complexes in the three transition groups. We may now discuss three major themes in the treatment of these groups: the spectrochemical series and the nephelauxetic series, both related to the "ligand field" transitions in the partly filled shell, and the series of apparent M.O. energies, as implied from the "electron transfer" spectra, where an electron is transferred to the partly filled shell.

In octahedral complexes, there is only one energy difference, Δ [also called $10Dq$ or $(E_1 - E_2)$] possible between the three equivalent γ_5 and two equivalent γ_3 orbitals. We see from Table IV

TABLE IV. The Octahedral (or Tetrahedral) M.O. Energy Difference Δ of Partly Filled d Shells and Interelectronic Repulsion Parameters. The Values of B_{55} Assuming Pure M.O. Configuration γ_5^a and B_{35} Assuming Pure $\gamma_5^a\gamma_3^b$ Are Derived Directly From Observed Distances between Absorption Band Maxima (see Table VIII). The Corrected Values of B_{55} and B_{35} Are Calculated from Tanabe and Sugano's Determinants, Assuming $C = 4B$, and the Corrected Values Can be Used for Estimating the Nephelauxetic Ratio β by Comparison with B in the Corresponding Gaseous Ion. Values of Δ, Which are Uncertain Because of Probable Distortions of the Regular Octahedral Symmetry, are Marked (J.T.) (Jahn–Teller-Effect). The Energy Levels in $5d^q$ Complexes, and in Certain Cr(III) and Ni(II) Complexes, Have Been Corrected for Effects of Intermediate Coupling. The Abbreviations Are $ox^{2-} = (COO)_2^{2-}$, en $= NH_2C_2H_4NH_2$, $dtp^- = (C_2H_5O)_2PS_2^-$, and $dsep^- = (C_2H_5O)_2PSe_2^-$. All Energies in cm^{-1}

			Δ	B_{55} pure γ_5^a	corr.	β_{55}	B_{35} pure $\gamma_5^a\gamma_3^b$	corr.	β_{35}
$3d$	Ti(III)	6 H_2O	19,000 (J.T.)	—	—	—	—	—	—
$3d^2$	V(III)	6 H_2O	18,400 (J.T.)	—	—	—	675	620	0.72
		6 $O^{2-}(Al_2O_3)$	18,600 (J.T.)	600	660	0.77	650	590	0.68
		6 F^-	15,900 (J.T.)	—	—	—	680	620	0.72
		6 urea	17,400 (J.T.)	—	—	—	—	—	—
		3 ox^{2-}	17,800 (J.T.)	585	640	0.74	665	550	0.64

TABLE IV (Continued)

				B_{55}			B_{35}		
			Δ	pure γ_5^a	corr.	β_{55}	pure $\gamma_5^a\gamma_3^b$	corr.	β_{35}
$3d^3$	V(II)	6 H_2O	12,350	(625)	(730)	(0.97)	515	690	0.93
	Cr(III)	6 H_2O	17,390	715	835	0.91	600	725	0.79
		6 $O^{2-}(Al_2O_3)$	18,000	690	800	0.87	550	645	0.70
		6 F^-	15,200	750	900	0.98	640	820	0.89
		6 Cl^-	13,800	645	770	0.84	435	510	0.56
		3 dtp$^-$	14,400	625	740	0.80	385	410	0.45
		3 dsep$^-$	13,700	600	710	0.77	325	340	0.37
		6 urea	16,000	690	810	0.88	550	660	0.72
		3 ox^{2-}	17,480	685	805	0.88	530	620	0.68
		6 NCS^-	17,800	—	—	—	510	570	0.62
		6 NH_3	21,550	730	830	0.90	580	650	0.71
		3 en	21,850	720	820	0.89	550	620	0.67
		6 CN^-	26,700	—	—	—	490	530	0.58
	Mn(IV)	6 F^-	21,750	775	900	0.84	540	600	0.56
$3d^5$	Mn(II)	6 H_2O	8,300	—	—	—	835	835	0.93
		6 O^{2-}	9,400	—	—	—	795	795	0.89
		6 F^-	7,800	—	—	—	845	845	0.94
		6 Cl^-	7,200	—	—	—	790	790	0.88
		6 S^{2-}	7,100	—	—	—	740	740	0.83
		4 Br^-	−3,000	—	—	—	765	765	0.86
		6 NCS^-	8,600	—	—	—	800	800	0.91
		3 en	9,900	—	—	—	790	790	0.88
	Fe(III)	6 H_2O	14,200	—	—	—	815	815	0.75
		6 F^-	13,900	—	—	—	845	845	0.78
		4 Cl^-	−5,000	—	—	—	625	625	0.58
		6 urea	13,000	—	—	—	775	775	0.72
		3 ox^{2-}	13,600	—	—	—	740	740	0.68
$3d^6$	Fe(II)	6 H_2O	9,400 (J.T.)	—	—	—	—	—	—
		6 CN^-	31,400	—	—	—	(375)	(400)	(0.45)
	Co(III)	6 F^-	13,100 (J.T.)	—	—	—	—	—	—
		6 H_2O	18,160	—	—	—	530	670	0.61
		3 ox^{2-}	18,020	—	—	—	450	540	0.49
		3 dtp$^-$	14,200	—	—	—	340	400	0.36
		6 NH_3	22,870	—	—	—	520	615	0.56
		3 en	23,160	—	—	—	505	590	0.53
		6 CN^-	33,450	—	—	—	410	460	0.42
$3d^7$	Co(II)	6 H_2O	9,300 (J.T.)	—	—	—	—	—	—
		6 $O^{2-}(MgO)$	9,600	—	—	—	—	820	0.85
		8 $F^-(CaF_2)$	−3,400	—	—	—	—	935	0.96
		4 $O^{2-}(ZnO)$	−3,800	—	—	—	—	750	0.78

TABLE IV (Continued)

				B_{55}			B_{35}		
			Δ	pure γ_5^a	corr.	β_{55}	pure $\gamma_5^a\gamma_3^b$	corr.	β_{35}
		4 Cl^-	−3,300	—	—	—	—	690	0.72
		4 Br^-	−3,000	—	—	—	—	660	0.68
		4 I^-	−2,800	—	—	—	—	600	0.62
		4 NCS^-	−4,500	—	—	—	—	(720)	(0.75)
		6 NH_3	10,100 (J.T.)	—	—	—	—	—	—
		3 en	10,400 (J.T.)	—	—	—	—	—	—
$3d^8$	Ni(II)	6 H_2O	8,500	—	—	—	—	940	0.89
		6 O^{2-}(MgO)	8,600	—	—	—	—	860	0.81
		6 F^-	7,300	—	—	—	—	960	0.91
		6 Cl^-	7,200	—	—	—	—	760	0.72
		6 Br^-	7,000	—	—	—	—	740	0.70
		3 gly^-	10,100	—	—	—	—	930	0.88
		6 NH_3	10,800	—	—	—	—	890	0.84
		3 en	11,500	—	—	—	—	850	0.81
$4d^3$	Mo(III)	6 Cl^-	19,200	430	470	0.78	390	440	0.73
	Tc(IV)	6 Cl^-	—	410	440	0.63	—	—	—
		6 Br^-	—	390	420	0.56	—	—	—
$4d^6$	Rh(III)	6 H_2O	27,000	—	—	—	455	530	0.73
		6 Cl^-	20,400	—	—	—	310	350	0.49
		6 Br^-	19,000	—	—	—	255	290	0.40
		3 ox^{2-}	26,400	—	—	—	—	—	—
		3 dtp^-	21,900	—	—	—	195	210	0.29
		6 NH_3	34,100	—	—	—	400	430	0.60
		3 en	34,600	—	—	—	395	420	0.59
		6 CN^-	45,000	—	—	—	(220)	(230)	(0.32)
	Pd(IV)	6 Cl^-	22,000	—	—	—	—	—	—
$5d^2$	Os(VI)	6 F^-	—	370	380	0.49	—	—	—
$5d^3$	Re(IV)	6 F^-	(32,000)	500	540	0.84	—	—	—
		6 Cl^-	27,500	400	430	0.67	—	—	—
		6 Br^-	—	370	400	0.63	—	—	—
	Ir(VI)	6 F^-	—	315	330	0.41	—	—	—
$5d^4$	Os(IV)	6 Cl^-	—	360	—	(0.50)	—	—	—
		6 Br^-	—	330	—	(0.46)	—	—	—
	Pt(VI)	6 F^-	—	260	—	(0.30)	—	—	—
$5d^6$	Ir(III)	6 Cl^-	25,000	—	—	—	250	300	0.46
		6 Br^-	23,100	—	—	—	210	250	0.38
		3 dtp^-	26,700	—	—	—	150	160	(0.24)
		3 en	41,400	—	—	—	—	—	—
	Pt(IV)	6 F^-	33,000	—	—	—	315	380	0.53
		6 Cl^-	29,000	—	—	—	—	—	—

that Δ is a function of the central atom, varying for the same ligand:

$$\mathrm{Mn(II)} < \mathrm{Ni(II)} < \mathrm{V(II)} < \mathrm{Fe(III)} < \mathrm{Cr(III)} < \mathrm{Co(III)} < \mathrm{Mn(IV)} < \mathrm{Mo(III)} < \mathrm{Rh(III)} < \mathrm{Pd(IV)} < \mathrm{Ir(III)} < \mathrm{Re(IV)} < \mathrm{Pt(IV)} \quad (23)$$

and a function of the ligands, varying for the same central atom:

$$\mathrm{I^-} < \mathrm{Br^-} < \mathrm{Cl^-} < \mathrm{F^-} < \text{urea} < \mathrm{ox^{2-}} \sim \mathrm{H_2O} \sim \mathrm{mal^{2-}} < \mathrm{SCN^-} < \mathrm{gly^-} < \mathrm{NH_3} \sim \text{py} < \text{en} \sim \text{den} < \text{dip} \sim \text{phen} < \mathrm{NO_2^-} \ll \mathrm{CN^-} \quad (24)$$

Tsuchida[235,247] found empirically the main part of Eq. (24) by studying the wave number of the first, spin-allowed ligand field band of the Co(III) complexes $Co(NH_3)_5X$ (for monodentate X) and $Co(NH_3)_4Y$ (for bidentate ligands Y such as ox^{2-}, en, etc.) and called the variation the "spectrochemical series." It is seen that the variation with the ligands is mainly a question of the coordinated atom

$$\mathrm{I} < \mathrm{Br} < \mathrm{Cl} < \mathrm{F} < \mathrm{O} < \mathrm{N} < \mathrm{C} \quad (25)$$

It can be remarked that some polyatomic ligands may coordinate with different atoms. Thus, the places marked for SCN^- and NO_2^- in (24) refer to nitrogen being bound to the central atom; *S*-bound thiocyanate is close to Cl^- and O-bound nitrite (as already discovered by Werner, preparing the red and yellow isomers of $Co(NH_3)_5NO_2^{2+}$) close to urea. However, sulfur cannot easily find a unique place in Eq. (25). Most S-containing ligands are close to Cl^-, but SO_3^{2-}, having only one lone-pair of electrons in analogy with NO_2^-, has a very late position close to the amines such as en.

It is interesting to note that the numerical variation of Δ is not exceedingly large. For Mn(II) to Pt(IV) in the same type of compounds (e.g. $KMnF_3$ and PtF_6^{2-}), the variation is within a factor 5, and the variation between bromide and nitrite in (24) is between 0.7 and 1.3 times the value of Δ for the hexaaquo ions. In the last comparison, CN^- was excepted; actually, the ratio is as high as 1.8 for $Co(CN)_6^{3-}$. The M.O. description has indeed given a very unified description of all the energy levels of octahedral complexes of partly filled *d*-shell atoms. For several years, this was ascribed by many authors (including the present one) to a very great reliability of the electrostatic model of the ligand field; but we must now realize that this success was only caused by the phenomenological introduction of electrostatic parameters as names for M.O. energy differences.

It was already a little suspicious that Δ is much larger for the oxidation number $+3$ than for $+2$ (while it is quite natural that the order of the three transition groups is $3d < 4d < 5d$ in Eq. (23), as caused by an increasing average radius of the partly filled shell), but the real difficulty with the electrostatic model is the variation of Δ with the ligands. Though Eq. (25) could be interpreted as a series of decreasing radii of the ligand atom, it was intolerable that neutral water and negatively charged OH^-, ox^{2-}, mal^{2-}, and O^{2-} itself all produce nearly the same values of Δ (within some 10%) for the same central ion.

Recently, it became clear that even worse objections to the electrostatic model could be made from the square-planar, diamagnetic d^8 complexes [some amine complexes of Ni(II), all known Pd(II) except the fluoride, and Pt(II)]. The empty orbital $(x^2 - y^2)$ (assuming the four ligands at the x,y axes) has much higher energy than the rest of the d shell. However, while the four other orbitals have approximately the same energy in complexes of water and (neutral) amines, the order is quite distinctly $(xy) > (xz,yz) > (z^2 - r^2/3)$ in halide complexes such as $PdCl_4^{2-}$, $PtCl_4^{2-}$, and $PtBr_4^{2-}$ (cf. Chatt, Gamlén, and Orgel[34]). No reasonable electrostatic model could produce this order of orbital energies, while the observed results are immediately obtained from M.O. arguments: the strong σ bonding present in all cases makes $(x^2 - y^2)$ the antibonding component, but does not disturb the energy of the other orbitals to first order. In the halide complexes, the π bonding increases the energy of (xy) twice as much [Eq. (41)] as that of the two degenerate orbitals (xz,yz).

Actually, a spectrochemical series can be defined from the first spin-allowed "ligand field" band of Pd(II) complexes:

$$\begin{aligned}&\mathrm{PdBr_4^{2-} < Pd(SCN)_4^{2-} < PdCl_4^{2-} < Pd(H_2O)_2Cl_2 < Pd\,ox_2^{2-}} <\\ &\quad \mathrm{Pd(H_2O)_4^{2+} < Pd\,mal_2^{2-} < Pd\,den\,Br^+ < Pd\,den\,Cl^+} <\\ &\quad \mathrm{Pd\,gly_2 < Pd\,den(OH)^+ < Pd\,den(NH_3)^{2+}}\\ &\quad \sim \mathrm{Pd(NH_3)_4^{2+} < Pd\,den_2^{2+} < Pd\,py_4^{2+} < Pd(CN)_4^{2-}}\end{aligned} \tag{26}$$

As a quite paradoxical fact, it may be mentioned that the wave number of the first spin-allowed band of Pd(II) is 1.03 to 1.10 times the wave number of the first spin-allowed ligand field band of the corresponding octahedral Rh(III) complex ($RhCl_6^{3-}$, Rh ox_3^{3-}, . . .). This can be partly explained by both types of transitions representing the differences between the effects of σ bonding (affecting the highest orbital) and of π bonding (affecting the next-highest orbital) on the partly filled shell.

In octahedral complexes with a component of the ligand field having tetragonal symmetry, the electrostatic model is also completely unsatisfactory. The deviations in cases like *trans*-Rh py_2 Cl_4^- and *trans*-Rh ox_2 Cl_2^{3-} are discussed by the present author,[124] and Griffith and Orgel[76] pointed out that π bonding from the chlorides in *trans*-Co en_2 Cl_2^+ can explain that the two orbitals (xz,yz) have higher energy than the third γ_5 from pure octahedral symmetry, viz. (xy). In an electrostatic model, this inversion could only occur if the quantity $\langle r^2 \rangle / R^2$ were above 1, i.e., if the partly filled shell were more extended than the ligand distance R from the central nucleus. Moffitt and Ballhausen[184] introduce three phenomenological parameters, Dq, Ds, and Dt, in the electrostatic model, taking care of linear combinations of the three independent M.O. energy differences [cf. Eq. (18)]. However, this description neglects the breakdown of any electrostatic picture which could produce the observed energy differences.

D. Nephelauxetic Effect and Covalent Bonding

However, even stronger arguments against the electrostatic model than those based on orbital energy differences and the spectrochemical series can be implied from the parameters of interelectronic repulsion. It is a fairly old idea that these parameters might be smaller in complexes than in the corresponding gaseous ion having the charge equal to the oxidation number of the metal in the complex. Thus, Abragam and Pryce[1] mentioned this possibility for $Co(H_2O)_6^{2+}$ in 1951, and Tanabe and Sugano[245] assume that such a decrease is necessary for a satisfactory description of trivalent $3d$ complexes, while it is less needed for the divalent ions. Owen[204] considered the decrease of term distances in both cases and found considerable values, 10 to 40 per cent.

Owen's explanation was based on the formation of antibonding M.O., delocalizing the partly filled shell out in the domain of the ligands. Orgel [197] suggested in 1955 a supplementary explanation, that electrons donated from the ligands and participating in formation of M.O. with arbitrary symmetry (for instance even γ_1 and odd γ_4) decrease the effective charge of the central ion. Orgel remarked the analogy with the smaller parameters of interelectronic repulsion in the gaseous Mn($3d^54s^2$) compared to gaseous Mn^{2+} ($3d^5$), since $Mn(H_2O)_6^{2+}$ is much closer to the former case.

The present author[134] suggested the names "symmetry-restricted covalency" and "central-field covalency" for the two types of explanation, and there is no doubt that both causes are effective, but their relative importance is difficult to evaluate. The two effects are called angular and radial polarization by Williams.[260] Until 1956 the phenomenon of decreased interelectronic repulsion had not been systematically studied as a function of the ligands for a given central ion. Schäffer and the present author[230] suggested the name the "nephelauxetic series" for the variation with central atom and ligands of the ratio β between the interelectronic repulsion parameters in a given complex and in the corresponding gaseous ion. Actually, the nephelauxetic series as a function of central atoms is

$$\begin{aligned}&\mathrm{Mn(II)} > \mathrm{V(II)} > \mathrm{Ni(II)} \sim \mathrm{Co(II)} > \mathrm{Mo(III)} > \mathrm{Cr(III)}\\ &\quad \sim \mathrm{Re(IV)} > \mathrm{Ir(III)} \sim \mathrm{Fe(III)} > \mathrm{Rh(III)} > \mathrm{Co(III)} > \\ &\quad \mathrm{Pt(IV)} \sim \mathrm{Mn(IV)} > \mathrm{Ir(VI)} > \mathrm{Pt(VI)}\end{aligned} \tag{27}$$

and as a function of ligands

$$\begin{aligned}F^- > H_2O > \mathrm{urea} > NH_3 > \mathrm{mal}^{2-} \sim \mathrm{en} \sim \mathrm{ox}^{2-}&\\ > SCN^- > Cl^- \sim CN^- \sim Br^- > I^-&\end{aligned} \tag{28}$$

Schäffer[229] demonstrated that different types of oxygen ligands may show a rather large spread in the nephelauxetic series, between F^- and Cl^-, and that sulfur ligands generally are close to Br^- or I^-. Disregarding this behavior of several oxo ligands, Eq. (28) can to a good approximation be re-written as

$$F > O > N > Cl > Br > I \sim S \tag{29}$$

The name of the nephelauxetic effect, meaning "expanding cloud" in Greek (as kindly proposed by Professor Kaj Barr, Copenhagen), is derived from the expansion of the radial function of the partly filled shell, which presumably is the cause of the relative decrease of the interelectronic repulsion parameters. As discussed on page 41, it is only approximately possible to calculate an average $\langle r^{-1} \rangle$ for the partly filled shell from the values of these parameters; on the other hand, the recent studies by Watson[256] indicate that the deviations in the proportionality factor to $\langle r^{-1} \rangle$, caused by correlation effects, have the same size in complexes and gaseous ions.

Concentrating the attention on either the central-field or the symmetry-restricted covalency, it is possible to interpret the observed values of β in two different ways: one is talking about an effective charge $Z_{\star}$ of the central ion, found by interpolation between the values of B (or another interelectronic repulsion parameter) in gaseous ions with the charges $z = +1, +2, +3, \cdots$. Actually, in the beginning of each transition group, B is proportional to $z + 1$, while it is proportional to $z + 3$ close to the end. Hence, a decrease of $Z_{\star}$ to two for $z = +3$ corresponds to a value of β of about 0.75 at the beginning and about 0.83 at the end of a transition group.

In octahedral (or tetrahedral) d^5 complexes with the high-spin ground state $^6\Gamma_1$ the transitions to the two terms $^4\Gamma_1$ and the lowest $^4\Gamma_3$ (the two quartets have the same energy[129] for $l = 2$) represent an exceptionally clear-cut case of the nephelauxetic effect, since the energy differences are independent of Δ. For $\Delta = 0$, as in the gaseous ions, the transitions are from ^6S to ^4G. Table V gives the wave numbers of these narrow bands (transitions inside $\gamma_5^3\gamma_3^2$) for a series of manganese(II) and iron(III) complexes, and for the gaseous Cr^+, Mn^{2+}, an extrapolated value for Fe^{3+}, and gaseous Mn. $Z_{\star}$ is seen to be 1.75 for the latter atom, containing two 4s electrons, and to vary between 1.8 and 0.8 in the Mn(II) and Fe(III) compounds. Presumably, the values of $Z_{\star}$ for the fluorides correspond fairly closely to the central-field covalency hypothesis. This does not mean that only 0.2 electron has invaded the manganese and 1.2 electron the iron central ion; we saw above that the effect of widely extended electrons, such as 4s in gaseous ions, is only a decrease of $Z_{\star}$ by some 0.1 to 0.2.

Actually, the nephelauxetic effect has been known in the lanthanides since 1926, when Ephraim and his co-workers[53]

TABLE V. The Energy Difference in cm^{-1} between $^6\Gamma_1$ and (the Nearly Degenerate) Levels $^4\Gamma_1$ and $^4\Gamma_3$ of $\gamma_5^3\gamma_3^2$ in Octahedral and Tetrahedral, High-Spin Manganese(II) and Iron(III) Complexes, and the Corresponding Energy Difference $^6S - {}^4G$ in Gaseous $3d^5$ Systems. The Small Superscripts Indicate Literature References

Mn^0 $[Ar]3d^54s^2$	25,279	$Mn(NCS)_6^{4-}$	24,000[130]
Cr^+ $[Ar]3d^5$	20,516	Mn $enta^{2-}$	24,200[122]
Mn^{2+} $[Ar]3d^5$	26,846	Mn en_3^{2+}	23,700[122]
Fe^{3+} extrapolated	32,800[134]	Mn py_2 Cl_2	23,800[3]
$Mn(H_2O)_6^{2+}$	25,000[93,122]	$Mn(H_2O)_4Cl_2$	24,650[3,221]
$MnO(6\ O^{2-})$	23,800[211]	$Fe(H_2O)_6^{3+}$	24,450[109]
$MnF_2(6\ F^-)$	25,300[101,244]	FeF_6^{3-}	25,350[232]
$MnCl_2(6\ Cl^-)$	23,700[205]	$FeCl_4^-$	18,800[64,182]
$MnBr_2(6\ Br^-)$	23,300[205]	Fe $urea_6^{3+}$	23,250[232]
$MnCl_4^{2-}$	23,200[40c,73]	Fe ox_3^{3-}	22,200[232]
$MnBr_4^{2-}$	23,000[73,122]	Fe mal_3^{3-}	22,800[232]

discovered a decrease of wave numbers of the narrow bands of R = Pr(III), Nd(III), Sm(III):

$$RF_3 > R(H_2O)_9^{3+} > \text{various R-oxo complexes} > RCl_3 > RBr_3 \sim R_2O_3 \qquad (30)$$

Ephraim assumed that the $4f$ electronic orbits are contracted due to strong electrostatic fields in the fluoride and the aquo ions, and that the orbits are expanded in covalent complexes such as the heavier halides and the acetylacetonate. At present, we can only retain the second part of the explanation; we do not foresee any specific contraction, and we assume that the energy differences of the gaseous R^{3+}, when they are known, will be even larger than in the fluoride. In Ephraim's time, it was not clear that the energy levels in lanthanides are separated by interelectronic repulsion in the partly filled $4f$ shell, and not by a difference in orbital extension, such as $1s$ and $2p$ in a hydrogen atom. The nephelauxetic effect has since been observed in rather many lanthanide complexes, also including gadolinium(III),[119] and in actinides.[136] Though β generally is only some 0.01 to 0.02 smaller than for the aquo ion, the effect is quite easy to measure, since the bands have such well-defined wave numbers. The corresponding values of $Z_\star$ above 2.8 do not, of course, reflect a very high charge of the central ion, as discussed above for Mn(II).

The other type of interpretation of β is a delocalization[241] of the partly filled shell into the ligands (in octahedral complexes due to formation of the σ antibonding γ_3 and π antibonding γ_5). The usual L.C.A.O. (linear combination of atomic orbitals) description is probably not very adequate for the actual M.O. formed; but if we make the simplification that the proportion x of the electron density (the squared wave function ψ^2) is distributed in the ligands, and $(1 - x)$ still resides in the central ion [that does not mean that the L.C.A.O. coefficients are $\sqrt{x}$ and $(1 - x)^{\frac{1}{2}}$, since the overlap integrals may be rather large], we would expect a relation of the form

$$\beta \cong (1 - x)^2 Z_\star / (Z_\star \text{ gaseous}) \qquad (31)$$

taking account of a possible variation of $Z_\star$ in the central ion part from the value in the gaseous ion. However, (31) assumes that the part of ψ concentrated on the ligands does not at all participate in the parameters of interelectronic repulsion. This is a rather complicated problem, since for M.O. without well-defined $l = 2$, the various K integrals and differences between J integrals may no longer be expressed in two parameters such as B and C. Actually, the number of necessary parameters for the diagonal elements in octahedral symmetry is nine and in very low symmetries twenty-five.[128,154] If non-diagonal elements are also considered, the number of parameters increases to 10 for octahedral and 120 for very low symmetry. If $l = 2$ was conserved, we would expect a further contribution to β of the order of magnitude

$$(2x - x^2)/\langle r^{-1}\rangle R \qquad (32)$$

from the interaction of the part x on the ligands (at the distance R) with itself and with the part $(1 - x)$ at the central ion, with $\langle r^{-1}\rangle$ pertaining to the partly filled shell of the gaseous ion.

Rather than consider the full set of nine J and K integrals in octahedral symmetry,[129] Koide and Pryce[153,205] suggest the use of a simpler extension of the parameters B and C from spherical symmetry. They assume that the γ_5 electrons are less delocalized on the ligands than the σ antibonding γ_3 electrons, and hence they write

$$\begin{aligned} B(\gamma_5,\gamma_5) &= B_0 \\ B(\gamma_5,\gamma_3) &= (1-\varepsilon)B_0 \\ B(\gamma_3,\gamma_3) &= (1-\varepsilon)^2 B_0 \end{aligned} \tag{33}$$

with a parameter B_0 possibly decreased compared to B of the gaseous ion, and a "covalency parameter" ε with a similar interpretation as x in Eq. (31), but only representing the difference in expansion of the γ_3 and γ_5 electrons.

Experimentally, there is no doubt that the distances $12B$ in d^3 and d^8 (Table VI) and $16B$ in diamagnetic d^6 systems, all

TABLE VI. Energy Levels for Octahedral and Tetrahedral Complexes, Assuming Tanabe and Sugano's Determinants, i.e., $l = 2$ and the Same Radial Function for γ_3 and γ_5. The Perturbation Theory Expression for the Subshell Configuration Intermixing is Indicated as a Multiple of B^2/Δ, Assuming $C = 4B$. The Quantities Implicitly Given by $x = 36B^2/(\Delta + 9B + x)$, $y = 36B^2/(\Delta - 9B + y)$ Are Especially Important for the Spin-Allowed Bands of High-Spin Complexes. It May be Remarked that in Octahedral d^8 Complexes, the Mixing of $\gamma_5^5\gamma_3^3$ and $\gamma_5^4\gamma_3^4$ in the Two $^3\Gamma_4$ is as Nearly Complete as to Give Approximately $+0.3\Delta + 1.5B$ and $+0.3\Delta + 13.5B$. The Reader May Derive this from the Expression for y When Δ is Close to $9B$

d^2	γ_5^2	$^3\Gamma_4$	$-0.8\Delta + 3B - x$
		$^1\Gamma_3$	$-0.8\Delta + 9B + 2C - 6B^2/\Delta$
		$^1\Gamma_5$	$-0.8\Delta + 9B + 2C - 12B^2/\Delta$
		$^1\Gamma_1$	$-0.8\Delta + 18B + 5C - 108B^2/\Delta$
	$\gamma_5\gamma_3$	$^3\Gamma_5$	$+0.2\Delta$
		$^3\Gamma_4$	$+0.2\Delta + 12B + x$
		. . .	
	γ_3^2	$^3\Gamma_2$	$+1.2\Delta$
		. . .	
d^3	γ_5^3	$^4\Gamma_2$	-1.2Δ
		$^2\Gamma_3$	$-1.2\Delta + 9B + 3C - 90B^2/\Delta$
		$^2\Gamma_4$	$-1.2\Delta + 9B + 3C - 24B^2/\Delta$
		$^2\Gamma_5$	$-1.2\Delta + 15B + 5C - 176B^2/\Delta$
	$\gamma_5^2\gamma_3$	$^4\Gamma_5$	-0.2Δ
		$^4\Gamma_4$	$-0.2\Delta + 12B - y$
		. . .	
	$\gamma_5\gamma_3^2$	$^4\Gamma_4$	$+0.8\Delta + 3B + y$

TABLE VI (Continued)

d^4	γ_5^4	$^3\Gamma_4$	$-1.6\Delta + 6B + 5C - 64B^2/\Delta$
		$^1\Gamma_3$	$-1.6\Delta + 12B + 7C - 82B^2/\Delta$
		$^1\Gamma_5$	$-1.6\Delta + 12B + 7C - 208B^2/\Delta$
		$^1\Gamma_1$	$-1.6\Delta + 21B + 10C - 436B^2/\Delta$
	$\gamma_5^3\gamma_3$	$^5\Gamma_3$	-0.6Δ
		$\cdots$	
	$\gamma_5^2\gamma_3^4$	$^5\Gamma_5$	$+0.4\Delta$
		$\cdots$	
d^5	γ_5^5	$^2\Gamma_5$	$-2\Delta + 15B + 10C - 140B^2/\Delta$
	$\gamma_5^4\gamma_3$	$^4\Gamma_4$	$-\Delta + 10B + 6C - 26B^2/\Delta$
		$^4\Gamma_5$	$-\Delta + 18B + 6C - 38B^2/\Delta$
		$\cdots$	
	$\gamma_5^3\gamma_3^2$	$^6\Gamma_1$	0
		$^4\Gamma_1$	$10B + 5C$
		$^4\Gamma_3$	$10B + 5C$
		$^4\Gamma_5$	$13B + 5C + \cdots$
		$^4\Gamma_3$	$17B + 5C$
		$^4\Gamma_4$	$19B + 7C - \cdots$
		$^4\Gamma_2$	$22B + 7C$
		$\cdots$	
d^6	γ_5^6	$^1\Gamma_1$	$-2.4\Delta + 5B + 8C - 120B^2/\Delta$
	$\gamma_5^5\gamma_3$	$^3\Gamma_4$	$-1.4\Delta + 5B + 5C - 70B^2/\Delta$
		$^3\Gamma_5$	$-1.4\Delta + 13B + 5C - 106B^2/\Delta$
		$^1\Gamma_4$	$-1.4\Delta + 5B + 7C - 34B^2/\Delta$
		$^1\Gamma_5$	$-1.4\Delta + 21B + 7C - 118B^2/\Delta$
	$\gamma_5^4\gamma_3^2$	$^5\Gamma_5$	-0.4Δ
		$\cdots$	
	$\gamma_5^3\gamma_3^3$	$^5\Gamma_3$	$+0.6\Delta$
		$\cdots$	
d^7	$\gamma_5^6\gamma_3$	$^2\Gamma_3$	$-1.8\Delta + 7B + 4C - 60B^2/\Delta$
	$\gamma_5^5\gamma_3^2$	$^4\Gamma_4$	$-0.8\Delta + 3B - x$
		$\cdots$	
	$\gamma_5^4\gamma_3^3$	$^4\Gamma_5$	$+0.2\Delta$
		$^4\Gamma_4$	$+0.2\Delta + 12B + x$
		$\cdots$	
	$\gamma_5^3\gamma_3^4$	$^4\Gamma_2$	$+1.2\Delta$
		$\cdots$	
d^8	$\gamma_5^6\gamma_3^2$	$^3\Gamma_2$	$-1\ 2\Delta$
		$^1\Gamma_3$	$-1.2\Delta + 8B + 2C - 6B^2/\Delta$
		$^1\Gamma_1$	$-1.2\Delta + 16B + 4C - 108B^2/\Delta$
	$\gamma_5^5\gamma_3^3$	$^3\Gamma_5$	-0.2Δ
		$^3\Gamma_4$	$-0.2\Delta + 12B - y$
		$^1\Gamma_5$	$-0.2\Delta + 8B + 2C - 12B^2/\Delta$
		$^1\Gamma_4$	$-0.2\Delta + 12B + 2C$
	$\gamma_5^4\gamma_3^4$	$^3\Gamma_4$	$+0.8\Delta + 3B + y$
		$\cdots$	

between spin-allowed bands, are all decreased more than the distances in d^3 proportional to $(3B + C)$. This is rationalized by Eq. (33), making the latter distances between spin-forbidden bands quantities of the type $(3B_0 + C_0)$ without ε-dependence, while $12B$ and $16B$ are of the type $(1 - \varepsilon)B_0$. A very good case is MnF_6^{2-}, where the spin-allowed bands give $\beta = 0.56$ ($B = 600$ cm^{-1}, while it is 1064 cm^{-1} in gaseous Mn^{4+}) though the spin-forbidden, internal transitions in γ_5^3 suggest $\beta = 0.84$ (see Table IV), i.e. ε of the order of magnitude 0.33. On the other hand, $MoCl_6^{3-}$ seems to have a very small ε, though B_0 is only 0.78 times the (extrapolated) value of B for gaseous Mo^{3+}. In the same way, one of the spin-forbidden transitions in octahedral nickel(II) complexes is of the $(1 - \varepsilon)^2B_0$ type of Eq. (33) and should have a smaller β than the $12B$-distance, if ε was significantly larger than zero. Actually, β for the two types of energy differences in Ni(II) is sensibly the same for a very large number of compounds.[20,117]

It may be concluded that the introduction of the parameter ε in Eq. (33) is only justified in the case of higher oxidation numbers of central ions, while in the less covalent complexes, a single β value seems to give a good description of the deviation from the gaseous ion. Table IV gives a series of such values of β marked β_{55} when determined from the internal γ_5^n transitions and β_{35} when Eq. (33) would suggest a decrease by the factor $(1 - \varepsilon)$. Two other problems must be handled for obtaining the values in Table IV: the ratio $C:B$, which has been fixed at 4, and the influence of M.O.-configuration intermixing. Dr. Claus Schäffer has contributed a large set of computations from the Tanabe–Sugano determinants, assuming that $\gamma_5^a\gamma_3^b$ has $l = 2$ and the same radial function for γ_5 and γ_3 (that would imply $\varepsilon = 0$).

Until now, we have talked as if the interelectronic repulsion parameters were exactly those we would derive from the Hartree–Fock solutions with well-defined configurations. As discussed on page 41, we know now that this is not the case even for gaseous ions. The reader might possibly conclude that all comparisons of the empirical values of the interelectronic repulsion parameters, as done in the nephelauxetic series, Eqs. (27) and (28), would yield no information on the actual spatial extension of the wave function of the partly filled shell. The conspicuous regularities found with the expected variation according to tendency of forming covalent bonds would then be regarded as possibly fortuitous.

The present author believes that the nephelauxetic effect is not subject to the same judgment as an empirical set of parameters, as is more evidently the case with the spectrochemical series. The main argument is that for gaseous ions, a closer inspection of especially Watson's results for $3d^n$ ions shows a rather surprising regularity: the Hartree–Fock solutions correspond to interelectronic repulsion parameters which are larger than the empirical values by a quantity which is nearly constant as a function of the ionic charge but depends on the multiplet term considered (the correction is generally larger for small values of L and S). Hence, the second-order effect of interelectronic correlation is nearly independent of the effective charge and the average $\langle r^{-1} \rangle$ of the partly filled shell, while the first-order effects of interelectronic repulsion are proportional to $\langle r^{-1} \rangle$. We may then hope that in M.O. configurations the second-order correlation effects decrease the energy of a certain symmetry type ${}^{2S+1}\Gamma_n$ by an amount nearly independent of the effective charges acting on the M.O. in the various atoms involved. It will presumably take a very long time before this assertion can be evaluated by actual calculations, but until then the empirical interelectronic repulsion parameters will serve as descriptive quantities, and we have good reasons for assuming a close connection with the actual values of $\langle r^{-1} \rangle$.

E. M.O. Treatment of Electron Transfer Spectra

At the present, the M.O. configuration description of polyatomic molecules and ions containing transition group elements has been most elaborated for octahedral complexes, especially hexahalide complexes MX_6 with $X = F^-, Cl^-, Br^-$, and I^- and

$M = 4d^0$	Mo(VI)	$M = 5d^0$	W(VI)
$4d^3$	Mo(III), Tc(IV)	$5d^2$	Os(VI)
$4d^4$	Ru(IV)	$5d^3$	Re(IV), Ir(VI)
$4d^5$	Ru(III)	$5d^4$	Os(IV), Pt(VI)
$4d^6$	Rh(III), Pd(IV)	$5d^5$	Os(III), Ir(IV)
		$5d^6$	Ir(III), Pt(IV)

Most of these complexes were discussed by the present author[137] in 1959 and the hexafluorides[138] in 1960. The variation of the wave numbers with M and X is much more regular than expected. Thus, for a given central ion (determining σ_r) the shift of the first electron transfer band with the halogen is always very close to:

$$\begin{array}{llll} \text{F}: & \sigma_r & \text{Cl}: & \sigma_r - 28{,}000\ \text{cm}^{-1} \\ \text{Br}: & \sigma_r - 34{,}000\ \text{cm}^{-1} & \text{I}: & \sigma_r - 44{,}000\ \text{cm}^{-1} \end{array} \tag{34}$$

In hexahalides with at least one empty place in the γ_5 subshell, i.e., all ions above except the diamagnetic γ_5^6 systems in the last line, a group of three to seven bands with a total spread of some 4000 to 8000 cm^{-1} occurs. These bands are relatively narrow, having half-widths (one side) δ of about 1000 cm^{-1} for chloride, 600 cm^{-1} for bromide, and 400 cm^{-1} for iodide complexes. The development of these band groups as function of halogen can be interpreted by the theory of intermediate coupling[137] because the electrodynamic and relativistic effects are no longer negligible in the iodide with $\zeta_{5p} = 5069$ cm^{-1}. The splitting of the band groups even in the fluoride and chloride complexes is caused by the interaction of the four sets of π orbitals (even γ_4, odd γ_5, even γ_5, odd γ_4) with the various l values of the central ion (see Table II) and the intermixing of λ values in the ligands.

At higher wave numbers, broader (δ 2000 to 4000 cm^{-1}) and much more intense bands occur. They are caused by the transition of odd γ_4 electrons (being mainly π, but to a certain extent also σ electrons) to the empty γ_3 subshell. In a few complexes ($PdCl_6^{2-}$, OsI_6^{2-}, $PtBr_6^{2-}$) it has been possible to observe the still stronger bands at still higher wave numbers caused by transfer of odd γ_4 (mainly σ) to the empty γ_3 subshell. The d^6 systems with filled γ_5 subshell do not, of course, exhibit the narrow bands $\pi \rightarrow \gamma_5$ but only the latter, broad $\pi \rightarrow \gamma_3$ and $\sigma \rightarrow \gamma_3$ bands. The variation of the quantity σ_r of Eq. (34) with the central ion is very regular. We may here apply a (rather small) correction for the interelectronic repulsion energy by the approximation for q electrons in the partly filled shell and the total spin S

$$Aq(q-1)/2 + D\{\langle S(S+1)\rangle - S(S+1)\} \tag{35}$$

In Eq. (35), A cannot be directly determined by experiment, but D is the effective spin-pairing energy (for a shell with $l = 2$, it is about $(5/2)B + C$). In the $4d$ and $5d$ groups, D is close to 2500 cm^{-1}. Table VII has been obtained with this correction. The average value of S for a given configuration $\langle S(S+1)\rangle$ in (35) can be expressed for an l-shell

TABLE VII. Values of σ_r From Eq. (34) For Hexahalide Complexes in Units of 1000 cm^{-1}. Some of the Δ Values (Marked ext.) are Extrapolated

		$\pi \rightarrow \gamma_5$	$\pi \rightarrow \gamma_3$	Δ from $\gamma_5 \rightarrow \gamma_3$
$4d^3$	Tc(IV)	52	—	—
$4d^4$	Ru(IV)	45	69	22 ext.
$4d^6$	Pd(IV)	—	60	22
$4d^6$	Rh(III)	—	70	20
$5d^0$	W(VI)	57	—	—
$5d^2$	Os(VI)	40	—	—
$5d^3$	Ir(VI)	31	—	—
$5d^4$	Pt(VI)	22	—	—
$5d^3$	Re(IV)	59	—	27
$5d^4$	Os(IV)	52	79	27 ext.
$5d^5$	Ir(IV)	47	74	28 ext.
$5d^6$	Pt(IV)	—	68	29
$5d^5$	Os(III)	62	—	25 ext.
$5d^6$	Ir(III)	—	78	25

$$q(q+2)/4 - (l+1)q(q-1)/(4l+1) \tag{36}$$

as will be justified in a review paper in *Solid State Physics*.[140]

A most surprising result is that Δ has very nearly the same value whether it is determined from internal "ligand field" transitions in the partly filled shell or from electron transfer transitions, i.e., the difference between $\pi \rightarrow \gamma_3$ and $\pi \rightarrow \gamma_5$ wave numbers. In other words, the contributions from the interelectronic repulsion energy cancel out in the two cases [except the spin-pairing energy related to D in Eq. (35)]. We cannot expect this always to be the case; but with this restriction in mind, we may identify the values of σ_r in Table VII with M.O. energies, all having the same, but unknown, zero-point, and being less positive the more difficult the excitation (or ionization) of the M.O. concerned.

These values of σ_r vary very regularly with the central ion:

(1) They decrease 15,000 cm^{-1} for each unit of increasing oxidation number in an isoelectronic series.

(2) They decrease 6000 cm^{-1} for hexachloro and 9000 cm^{-1} for hexafluoro complexes for each new electron in a partly filled γ_5 subshell with constant oxidation number.

(3) They are, under equal other conditions, 7000 cm^{-1} smaller for $4d$ than for $5d$ complexes.

When compared to gaseous ions, (1) is quite surprising. In most isoelectronic series the ionization energy increases some 100,000 cm^{-1} per unit of ionic charge. Hence, the complexes give an impression of having effective charges only increasing some 0.15 unit per unit of oxidation number. In the same way, the energy differences in Eq. (34) are very close to the differences in ionization energy of the *neutral* gaseous halogen atoms:

$$\begin{array}{ll} \mathrm{F}:\ 140{,}500\ \mathrm{cm}^{-1} & \mathrm{Cl}:\ 105{,}000\ \mathrm{cm}^{-1} \\ \mathrm{Br}:\ 95{,}500\ \mathrm{cm}^{-1} & \mathrm{I}:\ 84{,}300\ \mathrm{cm}^{-1} \end{array} \qquad (37)$$

The present author does not argue that Eq. (37) gives evidence that all the complexes considered are so covalent that the halogen atoms are effectively neutral; he will rather emphasize that the contribution of the Madelung energy to increase the ionization energy of the more negatively charged halogens in partly electrostatic compounds suffices to give nearly the same trend as in neutral halogen atoms.

In cases of more pronounced electrostatic bonding, the effects above may become strongly altered. The nearly constant trivalency of lanthanides is intimately connected with the fact that the drop of σ_r from trivalent to tetravalent compounds must be close to 80,000 cm^{-1}, not much below the difference in ionization energy of the corresponding gaseous ions. The lanthanides are characterized by a very great influence of spin-pairing energy on the stability of the half-filled shell $4f^7$; D of Eq. (35) is close to 6000 cm^{-1} [it is in this particular case the Racah parameter E^1].

The old idea of electronegativity has got a rather well-defined expression in the M.O. energy differences estimated from electron transfer spectra. Actually, Mulliken[189] defined the electronegativity of a given gaseous atom as the arithmetic mean of the ionization energy and electron affinity. The present author attempts to define a differential ionization energy $I(z)$ of each element as a function of the decimal fraction z indicating the effective charge. The ionization energy going from z to $(z + 1)$ is the integral of $I(z)$ between these two limits. Since I is close to being a linear function $a_0 + a_1 z$ (with a small parabolic correction $a_2 z^2$ and much smaller, higher-order contributions), this ionization energy is close to $I(z + \frac{1}{2})$. In the same way, Mulliken's electronegativity is approximately $I(0)$. As already pointed out by Daudel[12] and Haissinsky,[80] the electronegativity varies with the oxidation number of a given element. This is a more serious problem in inorganic chemistry than in the organic molecules generally containing a given element in approximately the same state of charge. The concept of electronegativity for $z = 0$ alone is obviously not sufficient for more electrostatic compounds. The present author suggests that a state of ionicity ξ in a binary compound MX_n is defined such that $z(M) = +n\xi$ and $z(X) = -\xi$. Taking the Madelung energy $-\alpha n \xi^2 / r_L$ into account, we would expect the minimum energy to occur at

$$I_M(n\xi) - I_X(\xi) - 2\alpha\xi/r_L = 0 \tag{38}$$

where the latter part (with r_L the M–X internuclear distance) represents the differential quotient of the Madelung energy (per atom of X) with respect to ξ. Dunn[47] discussed the charge distribution in $Fe(H_2O)_6^{3+}$ and other hexaaquo ions, but did not consider fractional charges or the Madelung energy, stabilizing the charge separation at small internuclear distances. Actually, Eq. (38) cannot be applied in a satisfactory way to neutral ligand molecules such as water.

When Eq. (38) is applied to transition group halides, plausible values for ξ are obtained. For instance, including some hypothetical compounds,

	$+n\xi$		$+n\xi$	
gaseous $NiCl_2$	1.2	gaseous (hypoth.) CrF_6	2.7	
solid $NiCl_2$	1.6	solid $MoCl_3$	2.5	
solid NiF_2	2.0	gaseous MoF_6	3.1	(39)
solid $CrCl_3$	2.3	solid (hypoth.) $CoCl_3$	2.0	
solid CrF_3	3.0	solid (hypoth.) CoI_3	1.6	

There is a lot of argument against the detailed validity of Eq. (38). The overlapping of ionic charge clouds (which are assumed to be points in the Madelung energy) and the influence of covalent bonding, having an appreciable differential quotient with respect to ξ, all contribute to this uncertainty; and correspondingly, the individual charges $+n\xi$ and $-\xi$ of the atoms are not very well defined. On the other hand, Eq. (38) generalizes the Born calculations on electrostatic energies of lattices. It is generally argued that some crystals, such as sodium chloride, have very closely the formation energy expected from bringing together the gaseous ions Na^+ and Cl^- and hence have very pure electrostatic bonding. We become convinced by Eq. (38) that intermediate cases of partly covalent, partly electrostatic bonding may occur in halides of higher oxidation numbers, though we may not expect to be able to calculate ξ very well from such a rough model.

We also get further evidence from Eq. (39) that the charge $+n\xi$ of the metallic atom has a considerable "buffer capacity" for changes in the oxidation number. In other words, as we always have expected, the vanadium charge in a series of compounds with the same ligand, VF_2, VF_3, VF_4, and VF_5, only increases slowly from perhaps 1.9 to 2.5. On the other hand, we have no strong evidence that the "buffering capacity" may be more than 100% effective in the way that the higher oxidation numbers of a given element would show smaller atomic charges $+n\xi$ than the lower oxidation numbers. In the case of the nephelauxetic effect, MnF_2 and FeF_3 have nearly the same values of the interelectronic repulsion parameters, indicating the same $\langle r^{-1} \rangle$, and PtF_6 has distinctly smaller values of $\langle r^{-1} \rangle$ than PtF_6^{2-}, or, considering an isoelectronic series, IrF_6 smaller $\langle r^{-1} \rangle$ than ReF_6^{2-}. However, this cannot directly be interpreted as a smaller atomic charge of iridium in IrF_6 than of rhenium in ReF_6^{2-}, since we do not only have central field covalency (see page 68) caused by expanded radial functions alone. The electron transfer spectra, as seen above, seem to indicate a small (15%) increase of atomic charge with increasing oxidation number.

At present, the M.O. description of the (regularly) tetrahedral complexes MX_4 is in a slightly less satisfactory state than that of the octahedral complexes. Helmholz and Wolfsberg[262] attempted in 1952 calculations of the energy levels of tetroxo ions such as

CrO_4^{2-} and MnO_4^-, while later the lower-symmetry, substituted ions such as CrO_3F^-, CrO_3Cl^-, and CrO_2Cl_2 were discussed.[94] This was the first case of what later has become known as the Helmholz–Wolfsberg method and it has been used by many authors on various complexes, but often with much less reliable assumptions than made by the original authors. By a reasonable choice of diagonal elements of atomic orbital energies and of overlap integrals between these atomic orbitals (determining the non-diagonal elements of orbital energy in the Helmholz–Wolfsberg method) the observed distribution of energy levels can be fairly well reproduced. However, as in several other applications of M.O. theory, we cannot obtain quantitative predictions, but we obtain useful and consistent explanations.

In the special case of MnO_4^-, there is no doubt now that all Helmholz's and Wolfsberg's detailed assignments of the transitions are incorrect. Recently, Carrington and Schonland[33] have demonstrated that the subshell γ_3 has lower energy than the subshell γ_5 in tetroxo complexes, as is also expected if the σ antibonding and π antibonding character of γ_5 produces a higher energy than the only π antibonding character of γ_3. The corresponding energy difference Δ can be evaluated from some transitions[32,139] and is $-13{,}000$ to $-16{,}000$ cm^{-1} for the $3d$ complexes and $-22{,}000$ cm^{-1} in RuO_4^{2-}. The electron transfer bands hence excite π and σ electrons to the empty or partly filled γ_3 and, at higher wave numbers, to the empty γ_5. An interesting question is the numerical value of the splitting between the three sets of π orbitals γ_4, γ_5, and γ_3 (there is no parity in the symmetry T_d, cf. page 43). We saw above that the corresponding splitting is 4000 to 8000 cm^{-1} in the hexahalides (perhaps slightly larger in the neutral hexafluorides). Among the tetroxides, the most unequivocal cases[33a] are the $4d^0$ systems TcO_4^- and RuO_4, both having two bands with a distance of 6000 cm^{-1}. These bands are caused by transitions of $\pi\gamma_4$ and $\pi\gamma_5$ electrons, respectively, to the empty γ_3 subshell. In the $3d$ group, it is much less clear whether the two strongest bands are caused[32] by transitions of $\pi\gamma_4$ to the two different subshells γ_3 and γ_5, or by $\pi\gamma_4 \rightarrow \gamma_3$ and $\pi\gamma_5 \rightarrow \gamma_3$ as suggested above for $4d^0$. The weak band groups around 16,000 cm^{-1} and the first strong band group at 19,000 cm^{-1} of MnO_4^- belong most probably to the same excited M.O. configuration, i.e., $^1\Gamma_4$ and $^1\Gamma_5$ of $\pi\gamma_4^{-1}\gamma_3$, and are then separated by surprisingly large effects of interelectronic repulsion. It is less easy to identify the broad shoulder at 28,300 and the band with vibrational structure at 32,200 cm^{-1}. If one of these bands is caused by $\pi\gamma_5 \rightarrow \gamma_3$, the splitting of the π group would be larger than in the hexahalides and in RuO_4. Though MnO_4^- has a shoulder at 44,000 cm^{-1}, it has no very strong band in the observed range, as would be expected of the transition $\gamma_5\sigma \rightarrow \gamma_5$.

The electron transfer spectra of tetrahalides are also known in some cases. Orgel[196] felt that there was something unexplained in the positions of the ligand field bands of $CoCl_4^{2-}$ and $FeCl_4^-$, and Low[172] invoked a mixing by the hemihedric ligand field (without center of inversion) of the configurations $3d^q$ and $3d^{q-1}4p$. Now, it must be concluded that the ligand field bands have low wave numbers due to the usual nephelauxetic effect of the halide, and that their intensities of course indicate some mixing of even and odd states. From the M.O. point of view, there is no mystery about the subshell γ_5 containing both $3d$ and $4p$ contributions from the central ion, as well as σ and π antibonding parts from the ligands; but the specific need for $4p$ mixing is only an artifact in the electrostatic ligand field description. In the same way, the use of the configurations $3d^{q-1}4p$ as source of vibronically induced intensity in the Laporte-forbidden ligand field bands of octahedral complexes[162] has been experimentally refused; the electron transfer configurations (odd $\pi)^{-1}3d^{q+1}$ or (odd $\sigma)^{-1}3d^{q+1}$ are much more important for the vibronically induced intensity. The values of Δ for tetrahedral halides are generally rather small, as seen in Table IV, confined between -2000 and -5000 cm^{-1}. Cobalt(II) and nickel(II) in oxide lattices have been studied recently,[178,226] and when the local micro-symmetry is tetrahedral, the spectra resemble closely the tetrahalides, with slightly more negative values of Δ.

Zaslow and Rundle[270] applied the Helmholz–Wolfsberg method to $FeCl_4^-$ and calculated a value of Δ close to zero. The electron transfer bands of about equal intensity at 27,500, 31,600, and 41,000 cm^{-1} are of course comparable to those of MnO_4^-. However, the spin-pairing energy is very important in $FeCl_4^-$; D is calculated from the ligand field bands to be 4000 cm^{-1}, and the transition from the ground state $\gamma_3^2\gamma_5^3$ (having $S = 5/2$) to the first excited states $\pi^{-1}\gamma_3^3\gamma_5^3$ and $\pi^{-1}\gamma_3^2\gamma_5^4$ (both having $S = 2$) costs

$(8/3)D = 10{,}700$ cm^{-1} according to the approximation expressed in (35). The first electron transfer band of $CoCl_4^{2-}$ (going from $\gamma_3^4\gamma_5^3$ to $\pi^{-1}\gamma_3^4\gamma_5^4$) is situated at 42,500 cm^{-1} and costs $(4/3)D = 5300$ cm^{-1} in spin-pairing energy.

We may ask for similar regularities as mentioned on page 77 for the hexahalides. The data given above for $CoCl_4^{2-}$ and $FeCl_4^-$ suggest that effect (1) of page 78 is to have σ_r at least 30,000 cm^{-1} smaller for trivalent than for isoelectronic divalent ions (e.g., Fe(III) and Mn(II)). Effect (2) is less easy to evaluate. Recent data by Dr. Scaife for VBr_4^- and the decrease of the wave numbers of electron transfer bands in the series $CoCl_4^{2-}$, $NiCl_4^{2-}$, and $CuCl_4^{2-}$ (of which unfortunately the latter two are strongly under suspicion for Jahn–Teller distortions) suggest a similar decrease of σ_r with electron number as in the hexahalides.

The tetroxides give much smaller values of effect (1), approximately 9000 cm^{-1} per unit of oxidation number (corresponding to a much smaller difference in electronegativity than between $FeCl_4^-$ and $MnCl_4^{2-}$), and similar values of effect (2). The homologous series CrO_4^{2-}, MoO_4^{2-}, WO_4^{2-} or MnO_4^-, TcO_4^-, ReO_4^- constitute one of the very rare cases where effect (3) can be compared in all three transition groups. Actually, the shift in σ_r values is 16,000 cm^{-1} from 3*d* to 4*d* and 8000 cm^{-1} from 4*d* to 5*d*. This agrees well with the chemical fact that, for a given oxidation number and electron configuration, 3*d* elements are much more oxidizing than the 4*d*, which again is more oxidizing than the similar 5*d* element. Incidentally, since Δ increases strongly with $3d < 4d < 5d$, both "ligand field" and electron transfer bands become hypsochromic, having higher wave number, with increasing number of the transition group.

The tetroxo ions might be used for inquiring into the position of oxygen in Eq. (34). Since WF_6 and WO_4^{2-} have comparable wave numbers of their first electron transfer band, as have even Os(VI) in OsF_6 and Os(VIII) in OsO_4, it might be argued that oxide is as slightly reducing as fluoride. However, this would be a premature conclusion, since halogen substitution, e.g., in CrO_3Cl^-, TcO_3Cl, and ReO_3Cl, does not have a very great bathochromic effect[27] and rather would suggest that oxygen is only some few thousand cm^{-1} above chlorine in Eq. (34). We may think of two explanations of this paradox: that the Madelung stabilization of the oxide ion is very dependent on the radius, and hence, on the oxidation number, of the metal ion; and that the π bonding effects strongly influence the M.O. energies of the partly filled shell. The former argument may be used considering the orange colour of Cs_2O (and low chemical stability of oxides of large cations with low charges), the white BaO with the first band[220] at 32,000 cm^{-1}, and La_2O_3 with bands at much higher energies. This is rather contrary to the usual variation with the oxidation number of the metal. However, in our case of the tetroxo ions, the influence of the oxygen on the energy of the π antibonding γ_3 must also be rather large. This can be inferred from the spectra of the protonated derivatives $Cr(OH)O_3^-$, $Mn(OH)O_3$, and $Re(OH)O_3$. As shown by Bailey, Carrington, Lott, and Symons,[6] all these hydroxytrioxo complexes have their first, rather weak, band some 3000 cm^{-1} below the first, stronger bands of the corresponding tetroxo complexes. The present author believes, as do Wolfsberg *et al*,[94] that the singly degenerate orbital, formed by the splitting of $\pi\gamma_4$ in the lower symmetry, has higher energy (and is the highest filled orbital in the examples) than the doubly degenerate part. The decrease of the energy difference between the highest filled orbital and the empty subshell γ_3 can hardly be ascribed to anything but a smaller π bonding effect of hydroxide ions (having only two lone-pairs) than of oxide ions (having three lone-pairs). The consequence would be that the empty γ_3 subshell should be approximately 12,000 cm^{-1} lower in $M(OH)_4$ than in MO_4, M being the same element with the same oxidation number. This rather surprising result is in accordance with other evidence from oxygen complexes with tetragonal symmetry, as will be discussed below.

F. Tetragonal Complexes

The ligand field transitions in diamagnetic d^8 complexes with the empty $(x^2 - y^2)$ orbital were discussed on page 66. The square-planar tetrahalides present electron-transfer bands at the following wave numbers in units of 1000 cm^{-1} (cf. Table VIII):

$4d^8$	$PdCl_4^{2-}$	35.8	44.9	$5d^8$	$PtCl_4^{2-}$	(43.1)	46.1		
	$PdBr_4^{2-}$	30.2	40.9		$PtBr_4^{2-}$	37.3			
	PdI_4^{2-}	20.5	24.5		PtI_4^{2-}	25.7	30.8	35.8	(40)
					$AuCl_4^-$	31.8	44.1		

TABLE VIII. Identified Energy Levels of Transition Group Complexes

Wavelength λ in mμ, Wave Number σ in kK ($= 1000\ \mathrm{cm}^{-1}$), Molar Extinction Coefficients ε, and Half-widths δ in kK [Usually towards Smaller Wave Numbers; Otherwise Marked (+)] of Maxima (Shoulders in Parentheses) and the Oscillator Strength P. The Complex Species are Characterized by the Electron Configuration of the Corresponding Gaseous Ion and by the Chemical Symbol of the Element, Followed by the Oxidation Number as a Roman Numeral in Parentheses.

			λ	σ	ε	δ	$P \cdot 10^{-5}$	
$3d^0$	V(V)	VO_4^{3-} [193]	272	36.8	8,000	broad	15,000	$\pi \rightarrow 3d\gamma_3$
	Cr(VI)	CrO_4^{2-} [32,262]	(435)	(23.0)		very weak		${}^1\Gamma_1 \rightarrow {}^1\Gamma_4(\pi\gamma_4)^{-1}$
			373	26.8	4,700	1.8	9,000	$\rightarrow {}^1\Gamma_5(\pi\gamma_4)^{-1}(3d\gamma_3)$
			273	36.6	3,900	irreg.	11,000	—
	Mn(VII)	MnO_4^- [19,262]	(625)	(16.0)	(100)	—	200	${}^1\Gamma_1 \rightarrow {}^1\Gamma_4(\pi\gamma_4)^{-1}(3d\gamma_3)$
			526	19.0	2,440	vibr. $\sigma_e = 0.75$	—	$\rightarrow {}^1\Gamma_5(\pi\gamma_4)^{-1}(3d\gamma_3)$
			(350)	(28.6)	(1,500)	—	—	$\rightarrow {}^1\Gamma_5(\pi\gamma_4)^{-1}(3d\gamma_5)$?
			310	32.3	1,730	vibr. $\sigma_e = 0.7$	—	$\rightarrow {}^1\Gamma_5(\pi\gamma_5)^{-1}(3d\gamma_3)$?
			(232)	(43.0)	(1,500)	—	—	$\rightarrow {}^1\Gamma_5(\sigma\gamma_5)^{-1}(3d\gamma_3)$?
$3d^1$	Ti(III)	$Ti(H_2O)_6^{3+}$ [90,123]	(575)	(17.4)	(2.5)	—	4	${}^2\Gamma_5 \rightarrow {}^2\Gamma_3$
			492	20.3	4.1	—	8	
		Ti urea$_6^{3+}$ [90]	625	16.0	10	—	15	${}^2\Gamma_5 \rightarrow {}^2\Gamma_3$
			570	17.5	10	—	15	
	V(IV)	$VO(H_2O)_x^{2+}$ [123]	768	13.1	16.5	1.4	20	$xy \rightarrow xz,yz$
			(625)	(16.0)	7.5	1.4	10	$xy \rightarrow (x^2 - y^2)$
			240	41.7	240	4.6	1,000	electron transfer?

TABLE VIII (Continued)

			λ	σ	ε	δ	$P \cdot 10^{-5}$	
		VO ox_2^{2-} [86,123]	792	12.6	25	2.2	50	$xy \rightarrow xz,yz$
			605	16.5	9	1.7	15	$xy \rightarrow (x^2 - y^2)$
			(340)	(29.4)	170	2.0	300	$xy \rightarrow (2z^2 - x^2 - y^2)$
			(260)	(38.5)	(1,000)	—	—	—
		VO enta^{2-} [123]	780	12.8	23	1.4	30	$xy \rightarrow xz,yz$
			582	17.2	19	1.4	25	$xy \rightarrow (x^2 - y^2)$
			(336)	(29.8)	22	2.0	40	$xy \rightarrow (2z^2 - x^2 - y^2)$
		VCl_4 gas [18a]	1,520	6.6	110	—	—	$^2\Gamma_3 \rightarrow {}^2\Gamma_5$
			1,270	7.8	(200)	—	—	
			1,080	9.2	230	—	—	
	Cr(V)	CrO_4^{3-} [31]	625	16.0	—	—	—	$3d\gamma_3 \rightarrow \gamma_5$
			355	28.2	—	—	—	$\pi\gamma_4 \rightarrow 3d\gamma_3$
	Mn(VI)	MnO_4^{2-} [19,32]	603	16.6	1,600	—	2,500	$3d\gamma_3 \rightarrow \gamma_5$?
			438	22.9	1,330	—	—	$\pi\gamma_4 \rightarrow 3d\gamma_3$
			353	28.3	1,640	—	—	$\pi\gamma_5 \rightarrow 3d\gamma'_3$?
			301	33.2	1,540	—	—	?
$3d^2$	V(III)	$V(H_2O)_6^{3+}$ [71,85]	585	17.1	5.6	1.6	8	$a^3\Gamma_4\gamma'^2_5 \rightarrow {}^3\Gamma_5\gamma_5\gamma'_3$
			396	25.2	8.3	1.6	12	$\rightarrow b^3\Gamma_4\gamma_5\gamma_3$
		$Al_2O_3(6\ O^{2-})$ [169,212]	1,140	8.77,				
			1,035	9.66	—	narrow	weak	$a^3\Gamma_4\gamma_5^2 \rightarrow {}^1\Gamma_{3,5}\gamma'^2_5$
			575	17.4	—	vibr. $\sigma_e = 0.17$	—	$\rightarrow {}^3\Gamma_5\gamma_5\gamma_3$
			475.7	21.02	—	line	weak	$\rightarrow {}^1\Gamma_1\gamma_5^2$
			397	25.2	—	broad	—	$\rightarrow b^3\Gamma_4\gamma'_5\gamma'_3$
		VF_6^{3-} [9]	(980)	(10.2)	—	—	weak	$a^3\Gamma_4\gamma'^2_5 \rightarrow {}^1\Gamma_{3,5}\gamma'^2_5$
			675	14.8	—	broad	—	$\rightarrow {}^3\Gamma_5\gamma'_5\gamma_3$
			435	23.0	—	broad	—	$\rightarrow b^3\Gamma_4\gamma_5\gamma'_3$

		V urea$_6^{3+}$ 85	615	16.2	11.9	1.7	20	$a^3\Gamma_4\gamma_5^2 \rightarrow {}^3\Gamma_5\gamma_5\gamma_3$
			414	24.2	15.2	—	30	$\rightarrow b^3\Gamma_4\gamma_5\gamma_3$
			(~370)	(27.0)	(8.0)			
		V ox$_3^{3-}$ 84,210a	608	16.45	—	—	—	$a^3\Gamma_4\gamma_5^2 \rightarrow {}^3\Gamma_5\gamma_5\gamma_3$
			425	23.5	—	—	—	$\rightarrow b^3\Gamma_4\gamma_5\gamma_3$
	Mn(V)	MnO$_4^{3-}$ 31	675	14.8	—	—	1,700	$\gamma_3^2 \rightarrow \gamma_3\gamma_5$
			328	30.5	—	—	11,000	$\pi\gamma_4 \rightarrow \gamma_3$
	Fe(VI)	FeO$_4^{2-}$ 31	790	12.7	—	—	900	$\gamma_3^2 \rightarrow \gamma_3\gamma_5$
			510	19.6	1,100	irreg.	3,500	$\pi \rightarrow \gamma_3$
$3d^3$	V(II)	V(H$_2$O)$_6^{2+}$ 12a,42,132	810	12.3	4.1	—	5	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
			(765)	(13.1)	weak	—	—	$\rightarrow {}^2\Gamma_{3,4}\gamma_5^3$?
			540	18.5	6.0	—	9	$\rightarrow a^4\Gamma_4\gamma_5^2\gamma_3$
			358	27.9	3	—	—	$\rightarrow b^4\Gamma_4\gamma_5\gamma_3^2$
			~295	34.0	(30)	broad	—	$3d\gamma_5 \rightarrow 4s\gamma_1$
	Cr(III)	Cr(H$_2$O)$_6^{3+}$ 52,108,161	(667)	(15.0)	(2)	narrow	0.2	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3\gamma_5^3$
			575	17.4	13.3	1.6	20	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
			407	24.6	15.3	2.1	28	$\rightarrow a^4\Gamma_4\gamma_5^2\gamma_3$
			264	37.8	4	broad	10	$\rightarrow b^4\Gamma_4\gamma_5\gamma_3^2$
		Al$_2$O$_3$(6 O^{2-}) 190,228,245	693	14.43	~5	two lines	(0.2)	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3\gamma_5^3$
			555	18.0	~40	1.3	(50)	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
			475.5	21.03	~5	three lines	(0.3)	$\rightarrow {}^2\Gamma_5\gamma_5^3$
			406	24.6	~60	1.4	(70)	$\rightarrow a^4\Gamma_4\gamma_5^2\gamma_3$
			(256)	(39.0)	~15	—	(20)	$\rightarrow b^4\Gamma_4\gamma_5\gamma_3^2$
		Cr$_2$O$_3$(6 O^{2-}) 178,190,228	705	14.2	weak	narrow	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3\gamma_5^3$
			603	16.6	—	irreg.	—	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
			461	21.7	—	—	—	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
		CrF$_6^{3-}$ 229,231	672	14.9	—	0.9	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
			638	15.7	—	narrow	—	$\rightarrow {}^2\Gamma_3\gamma_5^3$
			(610)	(16.4)	—	—	—	$\rightarrow {}^2\Gamma_4\gamma_5^3$
			(455)	(22.0)	—	—	—	$\rightarrow {}^2\Gamma_5\gamma_5^3$?
			440	22.7	—	1.7	—	$\rightarrow a^4\Gamma_4\gamma_5^2\gamma_3$
			291	34.4	—	broad	—	$\rightarrow b^4\Gamma_4\gamma_5\gamma_3^2$

TABLE VIII (Continued)

	λ	σ	ε	δ	$P \cdot 10^{-5}$	
$CrCl_3(6\ Cl^-)$ [190,231]	760	13.15	—	narrow	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3\gamma_5^3$
	732	13.7	—	—	—	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
	530	18.9	—	—	—	$\rightarrow a^4\Gamma_4\gamma_5^2\gamma_3$
Cr $urea_6^{3+}$ [229,231]	693	14.45	—	narrow	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3\gamma_5^3$
	(662)	15.1	—	—	—	$\rightarrow {}^2\Gamma_4\gamma_5^3$?
	620	16.15	—	1.3	—	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
	(478)	(20.95)	weak	—	—	$\rightarrow {}^2\Gamma_5\gamma_5^3$
	444	22.6	—	irreg.	—	$\rightarrow a^4\Gamma_4\gamma_5^2\gamma_3$
	291	34.4	—	broad	—	$\rightarrow b^4\Gamma_4\gamma_5\gamma_3^2$
Cr ox_3^{3-} [109,222,235]	697	14.35	5	0.06	0.3	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3\gamma_5^3$
	572	17.5	75	—	—	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
	419	23.85	81	—	—	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
$Cr(NCS)_6^{3-}$ [18,231]	564	17.7	160	—	—	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
	420	23.8	130	—	—	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
	309	32.4	25,000	—	—	internal SCN^-
	234	42.7	19,200	—	—	electron transfer?
Cr enta $(H_2O)^-$ [70a,114]	542	18.4	200	—	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
	391	25 6	120	—	—	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
Cr enta $(OH)^{2-}$ [70a,114]	578	17.3	120	—	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
	(420)	(23.8)	(80)	—	—	$\left.\begin{matrix} \\ \end{matrix}\right\} \rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
	396	25.3	90	—	—	
$Cr(NH_3)_6^{3+}$ [164,222,231]	656	15.3	—	lines	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3\gamma_5^3$
	465	21.55	30	1.6	45	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
	351.5	28.5	27	1.9	50	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
$Cr(NH_3)_5Cl^{2+}$ [164]	515	19.4	38	—	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^4\Gamma_5(t5)\gamma_5^2\gamma_3$
	(453)	(22.1)	(8)	—	—	$\rightarrow {}^4\Gamma_5(t4)\gamma_5^2\gamma_3$

	376	2.66	44	—	—	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
	~200	~50	(10,000)	—	—	electron transfer
$Cr(NH_3)_5I^{2+}$ 164	540	18.5	54	—	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^4\Gamma_5(t5)-\gamma_5^2\gamma_3$
	470	21.25	25	—	—	$\rightarrow {}^4\Gamma_5(t4)\gamma_5^2\gamma_3$
	291	34.4	4,000	—	—	$\pi \rightarrow (2z^2 - x^2 - y^2)$
	~222	~45	10,000	broad	—	$\sigma \rightarrow (2z^2 - x^2 - y^2)$
$Cr(NH_3)_5H_2O^{3+}$ 50,229	660	15.15	0.025	lines	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3\gamma_5^3$
	483	20.7	35	1.6	—	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
	360	27.8	29	1.7	—	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
Cr en_3^{3+} 164,224,261	668	14.9	0.6	lines	0.1	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3\gamma_5^3$
	642	15.5	0.3	lines	—	$\rightarrow {}^2\Gamma_4\gamma_5^3$?
	458	21.85	76	1.6	110	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
	351	28.45	60	1.9	110	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
cis-Cr $en_2(H_2O)_2^{3+}$ 261	484	20.65	67	—	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
	367	27.25	42	—	—	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
trans-Cr en_2 $(H_2O)_2^{3+}$ 261	508	19.7	22	—	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^4\Gamma_5(t5)\gamma_5^2\gamma_3$
	443	22.6	29	—	—	$\rightarrow {}^4\Gamma_5(t4)\gamma_5^2\gamma_3$
	361	27.7	39	—	—	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
Cr ox_2 en^- 225	690	14.5	2	narrow	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3\gamma_5^3$
	530	18.9	88	broad	—	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
	395	25.3	94	broad	—	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
	270	~37	800	broad	—	internal oxalate
$Cr(S_2P(OC_2H_5)_2)_3$ 141	(763)	(13.1)	(225)	—	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3\gamma_5^3$
	(732)	(13.6)	(320)	—	—	$\rightarrow {}^2\Gamma_4$?
	697	14.3	380	1.4	500	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
	536	18.6	270	1.3	—	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$ and ${}^2\Gamma_5\gamma_5^3$
	527	19.1	265	1.3	—	
	(347)	(28.8)	(5,000)	—	—	$\pi \rightarrow 3d\gamma_5$?
	(315)	(31.8)	(9,000)	—	—	
	280	35·7	15,200	(+) 1.7	22,000	$\pi \rightarrow 3d\gamma_3$

TABLE VIII (Continued)

			λ	σ	ε	δ	$P \cdot 10^{-5}$	
		$Cr(CN)_6^{3-}$ [24,231,264]	375	26.7	80	—	—	$^4\Gamma_2\gamma_5^3 \rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
			307	32.6	55	—	—	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
			264	37.9	7,000	—	—	$\pi \rightarrow \gamma_5$
	Mn(IV)	MnF_6^{2-} [133]	615	16.3	weak	vibr. irreg.	—	$^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3\gamma_5^3$
			460	21.75	—	—	—	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
			355	28.2	—	—	—	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
$3d^4$	Cr(II)	$Cr(H_2O)_6^{2+}$ [206,223]	710	14.1	4.7	broad, irreg.	—	$^5\Gamma_3\gamma_5^3\gamma_3 \rightarrow {}^5\Gamma_5\gamma_5^2\gamma_3^2$ (tetr.)
			(250)	($\sim$40)	(40)	—	—	$3d\gamma_5 \rightarrow 4s\gamma_1$
		Cr en_2^{2+} [206]	547	18.3	25	—	—	—
		$Mn(H_2O)_6^{3+}$ [83]	486	21.0	$\sim$10	—	—	—
		Mn ox_3^{3-} [141]	970	10.3	$\sim$1	—	—	$^5\Gamma_3\gamma_5^3\gamma_3 \rightarrow {}^3\Gamma$
			498	20.1	$\sim$100	—	—	$\rightarrow {}^5\Gamma_5\gamma_5^2\gamma_3^2$
		$Mn(CN)_6^{3-}$ [24]	326	30.7	2,500	—	—	$^3\Gamma_4\gamma_5^4 \rightarrow (\text{odd } \pi)^{-1}\gamma_5^5$
			270	37.0	1,400	—	—	—
$3d^5$	Mn(II)	$Mn(H_2O)_6^{2+}$ [93,109,122]	530	18.9	0.018	1.2	0.03	$^6\Gamma_1\gamma_5^3\gamma_3^2 \rightarrow a^4\Gamma_4\gamma_5^4\gamma_3$
			433	23.1	0.015	0.9	0.01	$\rightarrow a^4\Gamma_5\gamma_5^4\gamma_3$
			400.5	24.97	0.037	0.2	0.01	$\rightarrow {}^4\Gamma_1, {}^4\Gamma_3\gamma_5^3\gamma_3^2$
			(395)	25.3	0.019	0.2	—	
			376.8	26.54	0.002	—	0.001	$\rightarrow {}^2\Gamma\gamma_5^3\gamma_3^2$ or vibr. ?
			357	28.0	0.022	0.6	0.015	$\rightarrow b^4\Gamma_5\gamma_5^3\gamma_3^2$
			336	29.7	0.021	0.4	0.01	$\rightarrow b^4\Gamma_3\gamma_5^3\gamma_3^2$
			303	32.9	0.015	1.5	0.02	$\rightarrow b^4\Gamma_4$
			(262)	38.2	—	—	—	$\rightarrow {}^4\Gamma_2\gamma_5^3\gamma_3^2$?
			247	40.5	0.08	—	—	$\rightarrow c^4\Gamma_4$?
		$MnO(6\ O^{2-})$ [211]	610	16.4	—	broad	—	$^6\Gamma_1\gamma_5^3\gamma_3^2 \rightarrow a^4\Gamma_4\gamma_5^4\gamma_3$
			480	20.8	—	broad	—	$\rightarrow a^4\Gamma_5\gamma_5^4\gamma_3$
			420	23.8	—	narrow	—	$\rightarrow {}^4\Gamma_1, {}^4\Gamma_3\gamma_5^3\gamma_3^2$

$MnF_2(6\ F^-)$ 101,244	520	19.2	0.038	broad	—	${}^6\Gamma_1\gamma_5^3\gamma_3^2 \rightarrow a^4\Gamma_4\gamma_5^4\gamma_3$
	432	23.1	0.025	broad	—	$\rightarrow a^4\Gamma_5\gamma_5^4\gamma_3$
	395	25.3	0.15	narrow	—	$\rightarrow {}^4\Gamma_1, {}^4\Gamma_3\gamma_5^3\gamma_3^2$
	354	28.2	0.034	narrow	—	$\rightarrow b^4\Gamma_5\gamma_5^3\gamma_3^2$
	333	30.0	—	narrow	—	$\rightarrow b^4\Gamma_3\gamma_5^3\gamma_3^2$
	305	32.8	0.06	broad	—	$\rightarrow b^4\Gamma_4$
$MnCl_2(6\ Cl^-)$ 205	540	18.5	1.6	0.8	(1)	${}^6\Gamma_1\gamma_5^3\gamma_3^2 \rightarrow a^4\Gamma_4\gamma_5^4\gamma_3$
	455	22.0	3.5	0.8	(2)	$\rightarrow a^4\Gamma_5\gamma_5^4\gamma_3$
	422	23.7	5	vibr. irreg.	(1)	$\rightarrow {}^4\Gamma_1, {}^4\Gamma_3\gamma_5^3\gamma_3^2$
	372	26.9	6	vibr. irreg.	(1)	$\rightarrow b^4\Gamma_5\gamma_5^3\gamma_3^2$
	353.5	28.3	10	vibr. irreg.	(2)	$\rightarrow b^4\Gamma_3\gamma_5^3\gamma_3^2$
$MnBr_4^{2-}$ 40c,70c,73,122	(470)	(21.3)	1.5	0.9	1.2	${}^6\Gamma_1\gamma_3^2\gamma_5^3 \rightarrow a^4\Gamma_4\gamma_3^3\gamma_5^2$
	450	22.2	1.9	(+) 0.5	1	$\rightarrow a^4\Gamma_5$?
	434	23.05	0.9	(+) 0.35	0.3	$\rightarrow {}^4\Gamma_1, {}^4\Gamma_3\gamma_3^2\gamma_5^3$
	374	26.7	2.5	0.7	1.5	$\rightarrow b^4\Gamma_4, b^4\Gamma_5$
	361	27.7	3.3	(+) 0.4	1	$\rightarrow b^4\Gamma_3$
$MnS(6\ S^{2-})$ 141,180	600	16.7	—	—	—	${}^6\Gamma_1\gamma_5^3\gamma_3^2 \rightarrow a^4\Gamma_4\gamma_5^4\gamma_3$
	505	19.8	—	—	—	$\rightarrow a^4\Gamma_5\gamma_5^4\gamma_3$
	450	22.2	—	narrow	—	$\rightarrow {}^4\Gamma_1, {}^4\Gamma_3\gamma_5^3\gamma_3^2$
$ZnS(4\ S^{2-})$ 180	530	18.9	—	—	—	${}^6\Gamma_1\gamma_3^2\gamma_5^3 \rightarrow a^4\Gamma_4\gamma_3^3\gamma_5^2$
	498	20.1	—	—	—	$\rightarrow a^4\Gamma_5\gamma_3^3\gamma_5^2$
	463	21.6	—	—	—	$\rightarrow {}^4\Gamma_1, {}^4\Gamma_3\gamma_3^2\gamma_5^3$
	430	23.3	—	—	—	—
	389	25.9	—	—	—	—
$Mn(NCS)_6^{4-}$ 130	575	17.4	0.07	1.7	0.11	${}^6\Gamma_1\gamma_5^3\gamma_3^2 \rightarrow a^4\Gamma_4\gamma_5^4\gamma_3$
	454	22.05	0.085	—	0.1	$\rightarrow a^4\Gamma_5\gamma_5^4\gamma_3$
	417	24.0	0.21	0.55	0.11	$\rightarrow {}^4\Gamma_1, {}^4\Gamma_3\gamma_5^3\gamma_3^2$
	372	26.9	0.26	0.8	0.19	$b^4\Gamma_5\gamma_5^3\gamma_3^2$
	(350)	(28.6)	0.25	—	—	$\rightarrow b^4\Gamma_3\gamma_5^3\gamma_3^2$

TABLE VIII (Continued)

		λ	σ	ε	δ	$P \cdot 10^{-5}$	
	Mn enta^{2-} 122	532	18.8	0.044	1.5	0.06	${}^6\Gamma_1\gamma_5^3\gamma_3^2 \rightarrow a^4\Gamma_4\gamma_5^4\gamma_3$
		(471)	(21.2)	0.04	—	0.05	$\rightarrow a^4\Gamma_5\gamma_5^4\gamma_3$
		411	24.3	0.25	(−) 0.4, (+) 0.1	0.06	$\rightarrow {}^4\Gamma_1, {}^4\Gamma_3\gamma_5^3\gamma_3^2$
		367	27.2	0.03	—	0.02	$\rightarrow b^4\Gamma_5\gamma_5^3\gamma_3^2$
		343	29.2	0.03	—	0.02	$\rightarrow b^4\Gamma_3\gamma_5^3\gamma_3^2$
	Mn en$_3^{2+}$ 122	630	15.9	0.055	1.5	0.07	${}^6\Gamma_1\gamma_5^3\gamma_3^2 \rightarrow a^4\Gamma_4\gamma_5^4\gamma_3$
		494	20.3	0.063	1.5	0.08	$\rightarrow a^4\Gamma_5\gamma_5^4\gamma_3$
		422	23.7	0.10	0.3	0.03	$\rightarrow {}^4\Gamma_1, {}^4\Gamma_3\gamma_5^3\gamma_3^2$
		372	26.9	0.05	—	—	$\rightarrow b^4\Gamma_5\gamma_5^3\gamma_3^2$
Fe(III)	Fe(H$_2$O)$_6^{3+}$ 109,221	794	12.6	0.1	1.6	0.15	${}^6\Gamma_1\gamma_5^3\gamma_3^2 \rightarrow a^4\Gamma_4\gamma_5^4\gamma_3$
		540	18.5	0.1	2.3	0.2	$\rightarrow a^4\Gamma_5\gamma_5^4\gamma_3$
		(411)	(24.3)	0.4	0.5	0.2	$\left.\begin{matrix} \\ \\ \end{matrix}\right\} \rightarrow {}^4\Gamma_1, {}^4\Gamma_3\gamma_5^3\gamma$
		406	24.6	0.6	—	—	
		(364)	(27.5)	—	—	—	$\rightarrow b^4\Gamma_5\gamma_5^4\gamma_3$
		238	42.0	2,400	broad	—	$\rightarrow \pi^{-1}\gamma_5^4\gamma_3^2$
	FeF$_6^{3-}$ 232	705	14.2	—	broad	—	${}^6\Gamma_1\gamma_5^3\gamma_3^2 \rightarrow a^4\Gamma_4\gamma_5^4\gamma_3$
		508	19.7	low	broad	—	$\rightarrow a^4\Gamma_5\gamma_5^4\gamma_3$
		394	25.4	—	vibr. irreg.	—	$\rightarrow {}^4\Gamma_1, {}^4\Gamma_3\gamma_5^3\gamma_3^2$
		346.5	28.8	—	vibr. irreg.	—	$\rightarrow b^4\Gamma_5\gamma_5^3\gamma_3^2$
		332	30.2	weak	—	—	$\rightarrow b^4\Gamma_3\gamma_5^3\gamma_3^2$
	FeCl$_4^-$ 64,150,182	640	15.6	—	broad	—	${}^6\Gamma_1\gamma_3^2\gamma_5^3 \rightarrow a^4\Gamma_4\gamma_3^3\gamma_5^2$
		615	16.3	—	broad	—	$\rightarrow a^4\Gamma_5\gamma_3^3\gamma_5^2$
		531	18.8	—	narrow	—	$\rightarrow {}^4\Gamma_1, {}^4\Gamma_3\gamma_3^2\gamma_5^3$
		498	20.1	—	narrow	—	$\rightarrow b^4\Gamma_5\gamma_3^2\gamma_5^3$?
		447	22.4	—	narrow	—	$\rightarrow b^4\Gamma_3\gamma_3^2\gamma_5^3$?
		367	27.3	4,500	—	—	$\pi\gamma_4 \rightarrow \gamma_3$

			314	31.9	4,500	—	—	$\pi\gamma_5 \rightarrow \gamma_3$ or $\pi \rightarrow \gamma_5$
			243	41.1	6,000	—	—	electron transfer
		Fe urea_6^{3+} 232	798	12.5	—	broad	—	$^6\Gamma_1\gamma_5^3\gamma_3^2 \rightarrow a^4\Gamma_4\gamma_5^4\gamma_3$
			584	17.1	—	broad	—	$\rightarrow a^4\Gamma_5\gamma_5^4\gamma_3$
			433.5	23.1	—	narrow	—	$\rightarrow {}^4\Gamma_1, {}^4\Gamma_3\gamma_5^3\gamma_3^2$
			428.5	23.4	—	narrow	—	
		Fe ox_3^{3-} 232	930	10.7	—	broad	—	$^6\Gamma_1\gamma_5^3\gamma_3^2 \rightarrow a^4\Gamma_4\gamma_5^4\gamma_3$
			660	15.2	—	broad	—	$\rightarrow a^4\Gamma_5\gamma_5^4\gamma_3$
			(452)	(22.1)	—	narrow	—	$\rightarrow {}^4\Gamma_1, {}^4\Gamma_3\gamma_5^3\gamma_3^2$
		Fe(CN)_6^{3-} 24,116,150	418	23.9	1,000	irreg.	—	$^2\Gamma_5\gamma_5^5 \rightarrow (\text{odd } \pi)^{-1}\gamma_5^6$
			(322)	(31.1)	1,100	—	—	—
			304	32.9	1,600	—	—	—
			(282)	(35.5)	1,200	—	—	—
			260	38.5	1,200	—	—	—
			~210	~48	strong	—	—	odd $\pi \rightarrow \gamma_3$
$3d^6$	Fe(II)	$\text{Fe(H}_2\text{O)}_6^{2+}$ 40a,42,70,109	(1200)	(8.3)	—	—	—	$^5\Gamma_5\gamma_5^4\gamma_3^2 \rightarrow {}^5\Gamma_3\gamma_5^3\gamma_3^3$
			960	10.4	1.6	1.7	3	
			(695)	(14.4)	0.12	—	0.1	$\rightarrow {}^3\Gamma$?
			505	19.8	0.014	0.7	0.01	$\rightarrow {}^3\Gamma$
			474	21.1	0.01	0.2	0.002	$\rightarrow {}^3\Gamma$
			450	22.2	0.025	0.6	0.01	$\rightarrow {}^3\Gamma$
			386	25.9	0.04	0.8	0.03	$\rightarrow {}^3\Gamma$
			248	40.3	18	2.1	35	$3d\gamma_3 \rightarrow 4s\gamma_1$
		Fe dip_3^{2+} 125,259	522	19.1	8,600	—	—	$^1\Gamma_1\gamma_5^6 \rightarrow \gamma_5^5$ (dip $\pi^\star$)
			(495)	(20.2)	7,800	—	—	—
			(415)	(24.1)	2,400	—	—	—
			(388)	(25.8)	3,700	—	—	—
			351	28.5	6,500	—	—	internal dip
			299	33.5	70,000	—	—	internal dip
			(290)	(34.5)	60,000	—	—	internal dip
			247	40.5	32,000	—	—	internal dip

TABLE VIII (Continued)

		λ	σ	ε	δ	$P \cdot 10^{-5}$	
	Fe phen$_3^{2+}$ 125,259	510	19.6	11,200	—	—	$^1\Gamma_1\gamma_5^6 \rightarrow \gamma_5^5$ (phen $\pi^\star$)
		(485)	(21.0)	9,500	—	—	—
		(438)	(22.8)	7,300	—	—	—
		320	31.2	3,300	—	—	internal phen
		(290)	(34.4)	20,000	—	—	internal phen
		266	37.6	67,000	—	—	internal phen
		225	44.4	64,000	—	—	internal phen
	Fe(CN)$_6^{4-}$ 36	323	31.0	330	—	—	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
		(270)	(37.0)	(1,000)	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
		217	46.1	14,400	—	—	$\pi \rightarrow 3d\gamma_3$
Co(III)	CoF$_6^{3-}$ 40a	850	11.8	—	—	—	$\left.\right\}\ {}^5\Gamma_5\gamma_5^4\gamma_3^2 \rightarrow {}^5\Gamma_3\gamma_5^3\gamma_3^3$
		695	14.4	—	—	—	
	Co(H$_2$O)$_6^{3+}$ 231	606	16.5	40	—	80	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
		401.5	24.95	50	—	100	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	Co ox$_3^{3-}$ 149,231,235	602	16.6	125	—	200	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
		420	23.75	155	—	250	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
		243	41.1	26,000	—	80,000	electron transfer $\rightarrow \gamma_3$
	Co(NH$_3$)$_6^{3+}$ 109,163,247	770	13.0	0.23	1.7	0.4	$^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4\gamma_5^5\gamma_3$
		472	21.2	56	1.7	90	$\rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
		338.5	29.55	46	2.0	80	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
		~200	~50	(20,000)	—	80,000	σ odd $\gamma_4 \rightarrow 3d\gamma_3$
	Co(NH$_3$)$_5$F^{2+} 166	920	10.9	0.4	—	0.6	$^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4(t5)\gamma_5^5\gamma_3$
		(645)	(15.5)	(0.7)	—	1	$\rightarrow {}^3\Gamma$
		515	19.45	47	—	60	$\rightarrow {}^1\Gamma_4(t5)\gamma_5^5\gamma_3$
		(457)	(21.9)	(14)	—	20	$\rightarrow {}^1\Gamma_4(t2)\gamma_5^5\gamma_3$

	354	28.3	39	—	60	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	~200	~50	(20,000)	—	—	$\sigma \rightarrow 3d\gamma_3$
$Co(NH_3)_5Cl^{2+}$ [166]	877	11.4	0.4	—	—	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4(t5)\gamma_5^5\gamma_3$
	(658)	(15.2)	(0.8)	—	—	$\rightarrow {}^3\Gamma$
	535	18.7	50	—	—	$\rightarrow {}^1\Gamma_4(t5)\gamma_5^5\gamma_3$
	(468)	(21.4)	(11)	—	—	$\rightarrow {}^1\Gamma_4(t2)\gamma_5^5\gamma_3$
	363	27.5	47	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	(270)	(37.1)	600	—	—	$\pi Cl \rightarrow 3d(2z^2 - x^2 - y^2)$
	228	43.9	20,000	—	—	$\sigma Cl \rightarrow 3d(2z^2 - x^2 - y^2)$
$Co(NH_3)_5Br^{2+}$ [166,267]	928	10.8	5	—	—	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4(t5)\gamma_5^5\gamma_3$
	(675)	(14.8)	(4)	—	—	$\rightarrow {}^3\Gamma$
	550	18.2	58	—	—	$\rightarrow {}^1\Gamma_4(t5)\gamma_5^5\gamma_3$
	(470)	(21.3)	(12)	—	—	$\rightarrow {}^1\Gamma_4(t2)\gamma_5^5\gamma_3$
	313	32.0	850	—	—	$\pi Br \rightarrow 3d(2z^2 - x^2 - y^2)$
	253	39.5	18,500	—	—	$\sigma Br \rightarrow 3d(2z^2 - x^2 - y^2)$
$Co(NH_3)_5I^{2+}$ [166,267]	935	10.7	30	—	—	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4(t5)\gamma_5^5\gamma_3$
	(725)	(13.8)	(18)	—	—	$\rightarrow {}^3\Gamma$
	581	17.2	80	—	—	$\rightarrow {}^1\Gamma_4(t5)\gamma_5^5\gamma_3$
	383	26.1	2,700	—	—	$\pi I \rightarrow 3d(2z^2 - x^2 - y^2)$
	287	34.9	16,500	—	—	$\sigma I \rightarrow 3d(2z^2 - x^2 - y^2)$
$Co(NH_3)_5H_2O^{3+}$ [10,149]	485	20.6	42	—	—	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	340	29.4	42	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	192	52.2	25,000	—	—	electron transfer
$Co(NH_3)_5OH^{2+}$ [149,235]	502	19.9	66	—	—	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	369	27.1	72	—	—	—
	(290)	(34.5)	—	—	—	electron transfer
	210	47.6	11,000	—	—	electron transfer
$Co(NH_3)_4gly^{2+}$ [234]	492	20.3	72	1.9	120	${}^1\Gamma_1\gamma_6^5 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	347	28.8	85	2.0	150	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
$Co(NH_3)_4ox^+$ [235]	511	19.6	80	—	—	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	357	28.0	130	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$

TABLE VIII (Continued)

	λ	σ	ε	δ	$P \cdot 10^{-5}$	
Co en_3^{3+} [109,163,247]	730	13.7	0.34	1.7	0.5	$^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4\gamma_5^5\gamma_3$
	(570)	(17.5)	—	—	—	$\rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3$?
	465	21.55	88	1.6	130	$\rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	338	29.6	78	1.9	130	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	~200	~50	—	—	—	$\sigma \rightarrow 3d\gamma_3$
cis-Co $en_2Cl_2^+$ [10,22,165]	(605)	(~16.5)	(30)	—	—	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4(t2)\gamma_5^5\gamma_3$
	530	18.9	78	—	—	$\rightarrow {}^1\Gamma_4(t5)\gamma_5^5\gamma_3$
	376	25.6	70	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	312	(32.0)	(600)	—	—	$\pi Cl \rightarrow 3d\gamma_3$
	~240	~42	19,000	—	—	$\sigma Cl \rightarrow 3d\gamma_3$
trans-Co $en_2Cl_2^+$ [10,22,165]	618	16.2	34	—	—	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4(t5)\gamma_5^5\gamma_3$
	455	22.0	24	—	—	$\rightarrow {}^1\Gamma_4(t2)\gamma_5^5\gamma_3$
	388	25.8	36	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	308	(32.5)	(1,300)	—	—	$\pi Cl \rightarrow 3d\gamma_3$
	248	40.3	27,000	—	—	$\sigma Cl \rightarrow 3d\gamma_3$
Co den_2^{3+} [23]	467	21.4	125	—	200	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	341	29.5	85	—	150	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
$Co(CN)_6^{3-}$ [24,149,231]	309	32.4	200	—	—	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	256	39.0	140	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	~200	~50	(20,000)	—	—	odd $\pi \rightarrow 3d\gamma_3$
$Co(CO_3)_3^{3-}$ [114,187]	640	15.6	155	—	—	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	440	22.7	165	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	255	39.2	9,500	—	—	ligands $\rightarrow \gamma_3$
$Co(S_2COC_2H_5)_3$ [145,231]	612	16.1	270	—	—	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	482	20.8	360	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$

		$Co(S_2P(OC_2H_5)_2)_3$ [141]	738	13.55	450	1.2	500	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
			(526)	(19.0)	480	1.6	600	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
			406	24.6	6,500	2.2	13,000	$\pi \rightarrow 3d\gamma_3$
			335	29.9	18,000	2.6	45,000	$\sigma \rightarrow 3d\gamma_3$?
			233	43.0	9,500	3.9	35,000	—
		Co enta⁻ [114,187,235]	536	18.65	320	—	—	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
			380	26.3	230	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
			230	43.4	28,000	—	—	ligands → γ_3
$3d^7$	Co(II)	$Co(H_2O)_6^{2+}$ [100,108]	1,230	8.1	2	—	2	$a^4\Gamma_4\gamma_5^5\gamma_3^2 \rightarrow {}^4\Gamma_5\gamma_5^4\gamma_3^3$
			(880)	(11.3)	0.1	1.2	0.1	$\rightarrow {}^2\Gamma_3\gamma_5^6\gamma_3$
			(625)	(16.0)	0.3	1.2	0.3	$\rightarrow {}^4\Gamma_2\gamma_5^3\gamma_3^4$?
			514	19.4	4.6	1.2	5	$\rightarrow b^4\Gamma_4\gamma_5^4\gamma_3^3$
			(454)	(21.5)	(2.6)	1.2	3	$\rightarrow {}^2\Gamma$?
			(∼400)	(∼25)	0.2	—	—	$\rightarrow {}^2\Gamma$
		$MgO(6\ O^{2-})$ [170,205a]	1,180	8.5	strong	—	—	$a^4\Gamma_4\gamma_5^5\gamma_3^2 \rightarrow {}^4\Gamma_5\gamma_5^4\gamma_3^3$
			(1,100)	(9.1)	—	—	—	$\rightarrow {}^2\Gamma_3$?
			582	17.2	—	broad	—	$\rightarrow {}^4\Gamma_2$?
			535	18.7	—	narrow	—	$\rightarrow {}^2\Gamma_4$
			510	19.6	strong	broad	—	$\rightarrow b^4\Gamma_4\gamma_5^4\gamma_3^3$
			488	20.5	—	—	—	—
			410	24.4	weak	—	—	$\rightarrow {}^2\Gamma_5$
		$CaF_2(8\ F^-)$ [240]	3,100	3.2	—	—	—	${}^4\Gamma_2\gamma_3^4\gamma_5^3 \rightarrow {}^4\Gamma_5\gamma_3^3\gamma_5^4$
			2,850	3.5	—	—	—	
			1,700	5.9	—	—	—	$\rightarrow a^4\Gamma_4(\gamma_3^3\gamma_5^4 + \gamma_3^2\gamma_5^5)$
			1,520	6.6	—	—	—	
			562	17.8	—	—	—	$\rightarrow b^4\Gamma_4(\gamma_3^3\gamma_5^4 + \gamma_3^2\gamma_5^5)$ $+ {}^2\Gamma$ components $({}^2\Gamma_3, {}^2\Gamma_4, \gamma_3^4\gamma_5^3)$
			540	18.5	—	—	—	
			520	19.2	—	—	—	
			510	19.6	—	—	—	$\rightarrow {}^2\Gamma_1$
			490	20.4	—	—	—	$\rightarrow {}^2\Gamma_5$

TABLE VIII (Continued)

	λ	σ	ε	δ	$P \cdot 10^{-5}$	
ZnO(4 O^{2-})[178,,205a,226]	1,640	6.1	—	—	—	$^4\Gamma_2\gamma_3^4\gamma_5^3 \rightarrow a^4\Gamma_4$
	1,430	7.0	—	—	—	
	1,330	7.5	—	—	—	
	655	15.3	—	—	—	$\rightarrow b^4\Gamma_4(\gamma_3^3\gamma_5^4 + \gamma_3^2\gamma_5^5)$ $+ {}^2\Gamma_3, {}^2\Gamma_4(\gamma_3^4\gamma_5^3)$
	610	16.4	—	—	—	
	569	17.6	—	—	—	
$MgAl_2O_4$(4 O^{2-})[226]	627	15.95	—	—	—	$^4\Gamma_2(\gamma_3^4\gamma_5^3) \rightarrow b^4\Gamma_4(\gamma_3^3\gamma_5^4 + \gamma_3^2\gamma_5^5)$
	587	17.05	—	—	—	
	550	18.2	low	—	—	$\rightarrow {}^2\Gamma$
CdS(4 S^{2-})[205b]	1,900	5.2	—	—	120	$^4\Gamma_2\gamma_3^4\gamma_5^3 \rightarrow a^4\Gamma_4$
	1,560	6.5	—	—	—	
	735	13.6	—	—	800	$\rightarrow b^4\Gamma_4(\gamma_3^3\gamma_5^4 + \gamma_3^2\gamma_5^5)$ $+ {}^2\Gamma_3, {}^2\Gamma_4\gamma_3^4\gamma_5^3$
	708	14.1	—	—	—	
	690	14.5	—	—	—	
$CoCl_4^{2-}$[8,26a,40b,46,144,148]	1,620	6.2	~100	—	~50	$^4\Gamma_2(\gamma_3^4\gamma_5^3) \rightarrow a^4\Gamma_4$
	691	14.5	600	0.4	200	$\rightarrow b^4\Gamma_4(\gamma_3^3\gamma_5^4 + \gamma_3^2\gamma_5^5)$ + various doublets such as $^2\Gamma_3$ and $^2\Gamma_4$ of $\gamma_3^4\gamma_5^3$
	661	15.1	570	—	—	
	(643)	15.6	(400)	—	—	
	623	16.0	420	—	—	
	(610)	16.4	(280)	—	—	
	531	18.8	9	—	5	$\rightarrow {}^2\Gamma$
	505	19.8	4	—	2	$\rightarrow {}^2\Gamma$
	448	22.3	2	—	1	$\rightarrow {}^2\Gamma$
	414	24.2	0.4	—	—	$\rightarrow {}^2\Gamma$
	378	26.5	0.6	—	—	$\rightarrow {}^2\Gamma$
	320	31.3	0.4	—	—	$\rightarrow {}^2\Gamma$

			303	33.0	1.8	—	—	$\rightarrow {}^2\Gamma$
			235	42.5	3,000	—	—	$\pi\text{Cl} \rightarrow 3d$
		CoBr_4^{2-} 40b,46,54a,73	2,200	4.5	(80)	—	—	${}^4\Gamma_2(\gamma_3^4\gamma_5^3) \rightarrow a^4\Gamma_4$
			1,800	5.5	(100)	—	—	
			722	13.9	(850)	0.3	—	$\rightarrow b^4\Gamma_4(\gamma_3^3\gamma_5^4 + \gamma_3^2\gamma_5^5) + {}^2\Gamma_3, {}^2\Gamma_4\gamma_3^4\gamma_5^3$
			705	14.2	(800)	—	—	
			670	14.9	(600)	—	—	
			(645)	15.5	(400)	—	—	
		CoI_4^{2-} 40b,46,54a,73,99	2,350	4.3	(120)	—	—	${}^4\Gamma_2(\gamma_3^4\gamma_5^3) \rightarrow a^4\Gamma_4$
			1,900	5.3	(160)	—	—	
			785	12.7	—	—	—	$\rightarrow b^4\Gamma_4(\gamma_3^3\gamma_5^4 + \gamma_3^2\gamma_5^5) + {}^2\Gamma_3, {}^2\Gamma_4\gamma_3^4\gamma_5^3$
			713	14.0	—	—	—	
			685	14.6	—	—	—	
		Co(NCS)_4^{2-} 25,40b,130	1,230	8.1	250	—	—	${}^4\Gamma_2\gamma_3^4\gamma_5^3 \rightarrow a^4\Gamma_4$
			613	16.3	1800	irreg.	—	$\rightarrow b^4\Gamma_4(\gamma_3^3\gamma_5^4 + \gamma_3^2\gamma_5^5)$
			305	32.8	(10,000)	2.8	—	internal thiocyanate
		Co enta^{2-} 114	1,100	9.1	8	—	10	$a^4\Gamma_4\gamma_5^5\gamma_3^2 \rightarrow {}^4\Gamma_5\gamma_5^4\gamma_3^3$
			(615)	(16.3)	2	—	1	$\rightarrow {}^4\Gamma_2\gamma_5^3\gamma_3^4$?
			502	19.9	10	—	—	$\rightarrow b^4\Gamma_4\gamma_5^4\gamma_3^3 + {}^2\Gamma$
			485	20.6	12	narrow	20	
			465	21.5	13	—	—	
		$\text{Co(NH}_3)_6^{2+}$ 8	1,110	9.0	3	—	5	$a^4\Gamma_4\gamma_5^5\gamma_3^2 \rightarrow {}^4\Gamma_5\gamma_5^4\gamma_3^3$
			(540)	(18.5)	(4)	narrow	2	$\rightarrow {}^2\Gamma$?
			474	21.1	8	—	12	$\rightarrow b^4\Gamma_4\gamma_5^4\gamma_3^3$
		Co en_3^{2+} 8	1,070	9.3	5	—	8	$a^4\Gamma_4\gamma_5^5\gamma_3^2 \rightarrow {}^4\Gamma_5\gamma_5^4\gamma_3^3$
			(535)	(18.7)	(5)	narrow	3	$\rightarrow {}^2\Gamma$?
			461	21.7	14	1.5	20	$\rightarrow b^4\Gamma_4\gamma_5^4\gamma_3^3$
$3d^8$	Ni(II)	$\text{Ni(H}_2\text{O)}_6^{2+}$ 20,100,114,134,210	1,180	8.5	2.0	1.2	3	${}^3\Gamma_2\gamma_5^6\gamma_3^2 \rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
			715	13.8	2.1	1.2	3	$\rightarrow a^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
			658	15.2	(1.9)	1.2	—	$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
			544	18.4	0.05	0.5	0.02	$\rightarrow a^3\Gamma_4$ + water vibr.
			455	(22.0)	0.4	—	0.5	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3^3$
			395	25.3	5.2	1.5	7	$b^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$

TABLE VIII (Continued)

	λ	σ	ε	δ	$P \cdot 10^{-5}$	
$NiO(6\ O^{2-})$ [45,179]	1,140	8.8	(20)	—	30	$^3\Gamma_2\gamma_5^6\gamma_3^2 \rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
	720	13.9	(30)	—	—	$\rightarrow a^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
	638	15.2	weak	—	—	$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	(472)	(21.2)	—	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3^3$
	418	23.9	—	—	—	$\rightarrow b^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
	379	26.4	—	—	—	—
	343	29.2	—	broad	—	—
	~280	36	(10,000)	(5)	—	electron transfer
	~240	42	(12,000)	—	—	electron transfer
$MgO(6\ O^{2-})$ [157,170,205a,227]	1,160	8.6	—	—	—	$^3\Gamma_2\gamma_5^6\gamma_3^2 \rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
	740	13.5	—	—	—	$\rightarrow a^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
	660	14.9	—	narrow	—	$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	(464)	(21.6)	weak	vibr. $\sigma_e = 0.24$	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3^3$
	407	24.6	—	—	—	$\rightarrow b^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
$MgTiO_3(6\ O^{2-})$ [227]	835	12.0	—	—	—	$^3\Gamma_2\gamma_5^6\gamma_3^2 \rightarrow a^3\Gamma_4$
	750	13.3	weak	narrow	—	$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	(500)	(20)	—	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3^3$
	450	22.2	—	—	—	$\rightarrow b^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
$MgAl_2O_4(4\ O^{2-})$ [227]	(705)	(14.2)	weak	—	—	$a^3\Gamma_4\gamma_3^4\gamma_5^4 \rightarrow {}^1\Gamma_3, {}^1\Gamma_5\gamma_3^4\gamma_5^4$
	637	15.7	—	—	strong	$\left.\right\} \rightarrow b^3\Gamma_4(\gamma_3^3\gamma_5^5)$
	600	16.7	—	—		
$ZnO(4\ O^{2-})$ [178,205a,227]	1,190	8.4	—	—	—	$a^3\Gamma_4\gamma_3^4\gamma_5^4 \rightarrow {}^3\Gamma_2\gamma_3^2\gamma_5^6$
	815	12.3	weak	—	—	$\left.\right\} \rightarrow {}^1\Gamma_3, {}^1\Gamma_5\gamma_3^3\gamma_5^5$
	735	13.6	weak	—	—	
	660	15.2	—	—	—	$\left.\right\} \rightarrow b^3\Gamma_4(\gamma_3^3\gamma_5^5)$
	618	16.2	—	—	—	

$CdS(4\ S^{2-})$ [205b]	2,400	4.2	—	—	10	$a^3\Gamma_4\gamma_3^4\gamma_5^4 \rightarrow {}^3\Gamma_5\gamma_3^3\gamma_5^5$
	1,250	8.0	—	—	40	$\rightarrow {}^3\Gamma_2\gamma_3^2\gamma_5^6$
	980	10.2	—	—	70	$\rightarrow {}^4\Gamma_3, {}^1\Gamma_5\gamma_3^4\gamma_5^4$
	815	12.3	—	—	300	$\rightarrow b^3\Gamma_4\gamma_3^3\gamma_5^5$
	795	12·6	—	—	—	
	740	13·5	—	—	—	
$KNiF_3(6\ F^-)$ [141]	800	12.5	—	irreg.	—	${}^3\Gamma_2\gamma_5^6\gamma_3^2 \rightarrow a^3\Gamma_4$
	655	15.3	weak	narrow	—	$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	476	21.0	weak	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3^3$
	421	23.7	—	—	—	$\rightarrow b^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
$RbNiCl_3(6\ Cl^-)$ [2]	870	11.5	—	—	—	${}^3\Gamma_2\gamma_5^6\gamma_3^2 \rightarrow a^3\Gamma_4$ and ${}^1\Gamma_3$
	790	12.7	—	—	—	
	538	18.6	weak	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3^3$
	464	21.6	—	—	—	$\rightarrow b^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
$RbNiBr_3(6\ Br^-)$ [2]	960	(10.4)	—	—	—	${}^3\Gamma_2\gamma_5^6\gamma_3^2 \rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	870	11.5	—	—	—	$\rightarrow a^3\Gamma_4$
	578	17.3	weak	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3^3$
	495	20.2	—	—	—	$\rightarrow b^3\Gamma_4$
$NiCl_4^{2-}$ [70b,73,74a,79,131]	1,350	7·4	20	—	—	$a^3\Gamma_4\gamma_3^4\gamma_5^4 \rightarrow {}^3\Gamma_2\gamma_3^2\gamma_5^6$
	860	11·6	4	narrow	—	$\rightarrow {}^1\Gamma_3, {}^1\Gamma_5\gamma_3^4\gamma_5^4$
	705	14·2	210	0·7	—	$\rightarrow b^3\Gamma_4\gamma_3^3\gamma_5^5$
	655	15·3	200	—	—	
	(600)	(16·7)	(100)	—	—	
	260	38.5	3,600	broad	—	$\pi Cl \rightarrow 3d\gamma_5$
$Ni\ gly_2(H_2O)_2$ [175]	1,005	10.0	6.1	—	8	${}^3\Gamma_2\gamma_6^5\gamma_3^2 \rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
	(750)	13.3	weak	narrow	0.5	$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	620	16.1	4.2	—	5	$\rightarrow a^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
	370	27.0	6.8	—	10	$\rightarrow b^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
$Ni\ gly_3^-$ [114]	990	10.1	9.9	1.5	14	${}^3\Gamma_2\gamma_5^6\gamma_3^2 \rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
	763	13.1	2.0	0.3	0.6	$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	602	16.6	8.2	1.8	14	$\rightarrow a^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
	362	27.6	14.4	1.7	23	$\rightarrow b^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$

TABLE VIII (Continued)

	λ	σ	ε	δ	$P \cdot 10^{-5}$		
Ni enta^{2-} [117]	990	10.1	31	1.4	38	${}^3\Gamma_2\gamma_5^6\gamma_3^2$	$\rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
	790	12.7	(5)	narrow	3		$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	587	17.0	8.4	1.7	12		$\rightarrow a^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
	382	26.2	12.6	1.7	22		$\rightarrow b^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
Ni(NH$_3$)$_6^{2+}$ [114]	930	10.75	4.0	1.5	5.3	${}^3\Gamma_2\gamma_5^6\gamma_3^2$	$\rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
	760	13.15	0.5	0.5	0.2		$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	571	17.5	4.8	1.6	7		$\rightarrow a^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
	355	28.2	6.3	1.6	10		$\rightarrow b^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
Ni en$_3^{2+}$ [114]	890	11.2	7.3	1.3	10	${}^3\Gamma_2\gamma_5^6\gamma_3^2$	$\rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
	(805)	(12.4)	(5)	—	—		$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	545	18.35	6.7	1.6	10		$\rightarrow a^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
	(416)	(24.0)	(0.3)	—	15		$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3^3$
	345	29.0	8.6	1.7	14		$\rightarrow b^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
Ni en(H$_2$O)$_4^{2+}$ [7,117]	1,020	9.8	—	—	—	${}^3\Gamma_2\gamma_5^6\gamma_3^2$	$\rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
	734	13.6	2	narrow	—		$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	635	15.8	—	—	—		$\rightarrow a^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
	373	26.8	—	—	—		$\rightarrow b^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
Ni en ox$_2^{2-}$ [257]	1,010	9.9	8.9	1.4	12	${}^3\Gamma_2\gamma_5^6\gamma_3^2$	$\rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
	750	13.3	(3)	0.2	0.5		$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	612	16.3	13.3	1.5	20		$\rightarrow a^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
Ni en gly$_2$ [117]	955	10.5	8.7	1.7	14	${}^3\Gamma_2\gamma_5^6\gamma_3^2$	$\rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
	770	13.0	2.6	—	3		$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	577	17.3	8.0	1.8	13		$\rightarrow a^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
	356	28.1	12.7	1.8	23		$\rightarrow b^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
Ni en$_2$ gly$^+$ [117]	922	10.8	9.2	1.4	14	${}^3\Gamma_2\gamma_5^6\gamma_3^2$	$\rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
	(790)	(12.65)	4.2	—	5		$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$

	560	17.9	8.7	1.7	14	$\rightarrow a^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
	350	28.6	12.0	1.8	20	$\rightarrow b^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
Ni den$_2^{2+}$ [20,117]	872	11.5	12.9	1.5	20	$^3\Gamma_2\gamma_5^6\gamma_3^2 \rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
	805	(12.4)	—	—	—	$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	535	18.7	7.7	1.9	12	$\rightarrow a^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
	344	29.1	10.8	1.9	19	$\rightarrow b^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
Ni py$_4$(H$_2$O)$_2^{2+}$ [20]	985	10.15	3.7	1.9	6	$^3\Gamma_2\gamma_5^6\gamma_3^2 \rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
	743	13.5	1.2	narrow	—	$\rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	607	16.5	5.4	1.7	8	$\rightarrow a^3\Gamma_4$
	371	27.0	9.9	1.7	15	$\rightarrow b^3\Gamma_4$
Ni dip$_3^{2+}$ [114,125,215]	(868)	(11.5)	5.7	0.9	—	$^3\Gamma_2\gamma_5^6\gamma_3^2 \rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	790	12.65	7.1	1.2	9	$\rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
	521	19.2	11.6	1.7	18	$\rightarrow a^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
	(~385)	(~26)	(2,000)	broad	—	$3d\gamma_3 \rightarrow \pi^\star$ dip?
	318	32.4	40,000	—	—	internal dip
	296	33.8	42,000	—	—	internal dip
	245	40.8	32,000	—	—	internal dip
Ni phen$_3^{2+}$ [114,125,215]	(865)	(11.55)	5.5	1.0	—	$^3\Gamma_2\gamma_5^6\gamma_3^2 \rightarrow {}^1\Gamma_3\gamma_5^6\gamma_3^2$
	788	12.7	6.8	1.3	8.5	$\rightarrow {}^3\Gamma_5\gamma_5^5\gamma_3^3$
	519	19.3	11.9	1.6	18	$\rightarrow a^3\Gamma_4(\gamma_5^5\gamma_3^3 + \gamma_5^4\gamma_3^4)$
	(~385)	(~26)	(1,000)	broad	—	$3d\gamma_3 \rightarrow \pi^\star$ phen?
	344	29.1	1,500	—	—	internal phen
	327	30.6	2,400	—	—	internal phen
	(313)	(32.0)	3,300	—	—	internal phen
	294	34.0	28,000	—	—	internal phen
	270	37.1	78,000	—	—	internal phen
	227.5	44.0	93,000	—	—	internal phen
Ni en$_2^{2+}$ yellow[239]	450	22.2	(60)	—	—	$^1\Gamma_{t1} \rightarrow {}^1\Gamma$
Ni trien^{2+} yellow[127]	443	22.6	(80)	—	—	$^1\Gamma_{t1} \rightarrow {}^1\Gamma$

TABLE VIII (Continued)

			λ	σ	ε	δ	$P \cdot 10^{-5}$	
		Ni biuret$_2^{2-}$ [142]	465	21.5	50	1.8	80	$^1\Gamma_{t1} \rightarrow {}^1\Gamma$
			(415)	(24.1)	(30)	—	—	$^1\Gamma$
		Ni(CN)$_4^{2-}$ [24,26,158]	(364)	(27.5)	100	—	—	$^1\Gamma_{t1} \rightarrow {}^1\Gamma$
			312	32.0	800	—	—	—
			286	35.0	5,000	—	—	—
			267.5	37.4	11,000	—	—	—
$3d^9$	Cu(II)	Cu(H$_2$O)$_6^{2+}$ [16,100]	(1,060)	(9.4)	5	2	10	$^1\Gamma_{t3}(x^2 - y^2)^{-1}$ $\rightarrow {}^1\Gamma_{t1}(2z^2 - x^2 - y^2)^{-1}$
			795	12.6	13	1.9	25	$\rightarrow {}^1\Gamma_{t4}, {}^1\Gamma_{t5}(xy)^{-1}, (xz, yz)^{-1}$
			~200	~50	(1,600)	—	—	electron transfer to $(x^2 - y^2)$
		CuCl$_4^{2-}$ [14,44]	1,100	9	—	—	—	$3d^9 \rightarrow 3d^9$
			377	26.5	(1,700)	2.1	(3,000)	πCl → $3d$
			274	36.5	(4,000)	3.7	(14,000)	σCl → $3d$
			(230)	(43.5)	(1,400)	—	—	—
		CuBr$_4^{2-}$ [44,116]	1,250	8	—	—	—	$3d^9 \rightarrow 3d^9$
			588	17.0	1,000	1.5	—	πBr → $3d$
			512	19.5	2,100	(1.5)	—	
			~338	(29.6)	4,200	broad	—	σBr → $3d$?
			266	37.7	2,300	—	—	σBr → $3d$?
		CuSO$_4$ solid [16]	(1,150)	(8.7)	—	—	—	internal $3d^9$
			880	11.4	—	—	—	
		Cu gly$_2$, aq. [69,117,145]	635	15.8	40	—	—	internal $3d^9$
		Cu enta^{2-} [114,117]	734	13.6	91	2.0	185	internal $3d^9$
			(265)	(37.8)	(2,600)	—	—	electron transfer → $3d$
		Cu(NH$_3$)$_4^{2+}$ [16]	590	16.9	52	2.5	120	$^1\Gamma_{t3}(x^2 - y^2)^{-1} \rightarrow {}^1\Gamma_{t1}, {}^1\Gamma_{t4}, {}^1\Gamma_{t5}$

		$Cu(NH_3)_5^{2+}$ [16]	(850)	(11.8)	30	2	60	${}^1\Gamma_{t3} \rightarrow {}^1\Gamma_{t1}(2z^2 - x^2 - y^2)^{-1}$
			640	15.6	82	2.2	170	$\rightarrow {}^1\Gamma_{t4}, {}^1\Gamma_{t5}$
		Cu en_2^{2+} [16]	549	18.2	63	2.4	140	${}^1\Gamma_{t3}(x^2 - y^2)^{-1} \rightarrow {}^1\Gamma_{t1}, {}^1\Gamma_{t4}, {}^1\Gamma_{t5}$
		Cu den $(H_2O)^{2+}$ [117]	611	16.3	74	2.3	170	${}^1\Gamma_{t3} \rightarrow {}^1\Gamma_{t1}, {}^1\Gamma_{t4}, {}^1\Gamma_{t5}$
		Cu den $(NH_3)^{2+}$ [117]	576	17.4	84	2.6	200	${}^1\Gamma_{t3} \rightarrow {}^1\Gamma_{t1}, {}^1\Gamma_{t4}, {}^1\Gamma_{t5}$
		Cu den_2^{2+} [117]	(850)	(11.8)	(70)	1.8	120	${}^1\Gamma_{t3} \rightarrow {}^1\Gamma_{t1}$
			630	15.9	106	2.6	250	${}^1\Gamma_{t3} \rightarrow {}^1\Gamma_{t4}, {}^1\Gamma_{t5}$
		Cu $trien^{2+}$ [142,217b]	575	17.4	150	—	350	${}^1\Gamma_{t3} \rightarrow {}^1\Gamma_{t1}, {}^1\Gamma_{t4}, {}^1\Gamma_{t5}$
		Cu $biuret_2^{2-}$ [142]	505	19.8	40	—	100	${}^1\Gamma_{t3} \rightarrow {}^1\Gamma_{t5}$
		Cu dip_3^{2+} [111]	~1,180	8.5	weak	—	—	$3d^9 \rightarrow 3d^9$
			680	14.7	60	—	—	
		Cu $phen_3^{2+}$ [114]	~1,230	8	weak	—	—	$3d^9 \rightarrow 3d^9$
			680	14.7	50	—	—	
$3d^{10}$	Cu(I)	Cu dip_2^+ [259]	435	23.0	4,550	—	—	$3d\gamma_5 \rightarrow \pi^\star$ dip
		Cu $phen_2^+$ [259]	435	23.0	7,040	—	—	$3d\gamma_5 \rightarrow \pi^\star$ phen
		$Cu(CN)_4^{3-}$ [236]	295	33.9	170	—	—	$3d\gamma_5 \rightarrow 4s\gamma_1$?
			235	42.5	11,000	—	—	?
$4d^0$	Mo(VI)	MoO_4^{2-} [31]	227	44.0	—	—	—	$\pi \rightarrow 4d\gamma_3$
		MoF_6 gas [246]	185	54.0	—	vibr. $\sigma_c = 0.64$	—	$\pi \rightarrow 4d\gamma_5$
	Tc(VII)	TcO_4^- [21,21a]	289	34.6	2,000	vibr. σ_c	—	$\pi\gamma_4 \rightarrow 4d\gamma_3$
			247	40.5	4,000	—	—	$\pi\gamma_5 \rightarrow 4d\gamma_3$
			220	45.5	(1,800)	—	—	?
	Ru(VIII)	RuO_4 gas [38,179]	385	26.0	900	vibr. σ_c	—	$\pi\gamma_4 \rightarrow 4d\gamma_3$
			310	32.3	3,000	—	—	$\pi\gamma_5 \rightarrow 4d\gamma_3$
			(245)	(41)	(1,200)	—	—	?
$4d^1$	Mo(V)	$MoOCl_5^{2-}$ [123]	712	14.05	16	1.5	22	${}^2\Gamma_{t4}(xy) \rightarrow {}^2\Gamma_{t5}(xz, yz)$
			445	22.5	14	1.1	14	$\rightarrow {}^2\Gamma_{t3}(x^2 - y^2)$
			355	28.2	500	1.4	650	even $\pi \rightarrow 4d$
			310	32.2	4,400	1.6	6,500	odd $\pi \rightarrow 4d$
			240	40.7	5,500	2.1	11,000	odd $\pi \rightarrow 4d$

TABLE VIII (Continued)

			λ	σ	ε	δ	$P \cdot 10^{-5}$	
	Ru(VII)	RuO_4^- 38	385	26.0	2,300	broad	—	$4d\gamma_3 \rightarrow 4d\gamma_5$?
			310	32.3	2,400	vibr.	—	$\pi\gamma_4 \rightarrow 4d\gamma_3$?
$4d^2$	Ru(VI)	RuO_4^{2-} 38	463	21.6	1,800	2.2	4,000	$\gamma_3^2 \rightarrow \gamma_3\gamma_5$?
			(375)	(26.7)	(1,000)	broad	—	?
		$RuO_2Cl_4^{2-}$ 56	328	30.5	5,000	3.0	14,000	$(4dxy)^2 \rightarrow (\pi Cl)^{-1}(xy)^2(xz,yz)$
$4d^3$	Mo(III)	$MoCl_6^{3-}$ 88,123,130,217a	1,035	9.7	0.5	0.5	0.2	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3, {}^2\Gamma_4\gamma_5^3$
			676	14.8	1.7	0.3	0.5	$\rightarrow {}^2\Gamma_5\gamma_5^3$
			522	19.2	25	1.5	35	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
			418	23.9	35	—	50	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
			221	45.3	(5,000)	—	—	$\pi Cl \rightarrow 4d\gamma_5$
		$MoCl_5(H_2O)^{2-}$ 123,130	1,050	9.5	—	0.4	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3, {}^2\Gamma_4\gamma_5^3$
			678	14.75	—	0.3	—	$\rightarrow {}^2\Gamma_5\gamma_5^3$
			(652)	(15.35)	—	—	—	
			506	19.8	—	—	—	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$
			406	24.6	—	—	—	$\rightarrow {}^4\Gamma_4\gamma_5^2\gamma_3$
	Tc(IV)	$TcCl_6^{2-}$ 27,194	700	14.3	3	narrow	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_5\gamma_5^3$
			(400)	(25)	(1,000)	—	—	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$?
			340	29.4	(12,000)	—	—	$\pi Cl \rightarrow 4d\gamma_5$
			~300	~33	(8,000)	—	—	$\pi Cl \rightarrow 4d\gamma_5$
			240	41.7	(18,000)	—	—	$\pi Cl \rightarrow 4d\gamma_3$?
		$TcBr_6^{2-}$ 194	1,130	8.85	1.1	narrow	—	${}^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3, {}^2\Gamma_4\gamma_5^3$
			1,060	9.45	1.5	narrow	—	
			740	13.5	10.6	narrow	—	$\rightarrow {}^2\Gamma_5\gamma_5^3$
			(515)	(19.4)	(250)	—	—	even $\pi Br \rightarrow 4d\gamma_5$?
			445	22.5	(2,000)	—	—	odd $\pi Br \rightarrow 4d\gamma_5$
			383	26.1	(3,000)	—	—	odd $\pi Br \rightarrow 4d\gamma_5$

$4d^4$	Ru(IV)	$RuCl_6^{2-}$ [56,137]	583	17.15	660	1.0	600	$^3\Gamma_4\gamma_5^4 \rightarrow (\text{even } \pi\gamma_4)^{-1}\gamma_5^5$
			486	20.3	4,400	0.9	3,600	odd $\pi\gamma_5 \rightarrow 4d\gamma_5$
			(436)	(22.9)	(3,500)	—	(1,000)	odd $\pi\gamma_4 \rightarrow 4d\gamma_5$
			(406)	(24.6)	(3,000)	—	(2,000)	
			(278)	(36.0)	(12,000)	3.3	(35,000)	odd $\pi\gamma_4 \rightarrow 4d\gamma_3$?
			(244)	(41.0)	(18,000)	—	—	
$4d^5$	Ru(III)	$Ru(H_2O)_6^{3+}$ [29]	~400	~25	~50	—	—	$^2\Gamma_5\gamma_5^5 \rightarrow {}^2\Gamma\gamma_5^4\gamma_3$
			225	44.5	2,300	—	—	$\pi \rightarrow 4d\gamma_5$
		$RuCl_6^{3-}$ [116,137]	528	19.0	40	2.0	70	$^2\Gamma_5\gamma_5^5 \rightarrow {}^2\Gamma\gamma_5^4\gamma_3$
			(390)	25.6	600	—	(800)	even $\pi\gamma_4 \rightarrow 4d\gamma_5$
			349	28.7	2,200	1.3	2,500	odd $\pi\gamma_5 \rightarrow 4d\gamma_5$
			309	32.4	1,700	—	(2,000)	odd $\pi\gamma_4 \rightarrow 4d\gamma_5$
			229	43.6	16,000	3.8	55,000	odd $\pi\gamma_4 \rightarrow 4d\gamma_3$
		$RuBr_6^{3-}$ [137]	(610)	(16.4)	130	—	—	?
			(518)	(19.3)	720	—	—	—
			(470)	(21.3)	1,420	—	—	—
			445	22.5	1,810	—	—	—
			435	23.0	1,800	—	—	—
			397	25.2	2,220	—	—	—
			(367)	(27.2)	1,780	—	—	—
			(286)	(35.0)	(14,000)	3.4	—	odd $\pi\gamma_4 \rightarrow 4d\gamma_3$
		$Ru(H_2O)_5Cl^{2+}$ [29]	315	31.8	680	—	—	$\pi Cl \rightarrow 4d\gamma_5$
		$Ru(NH_3)_5Cl^{2+}$ [87]	328	30.5	1,930	—	—	$\pi Cl \rightarrow 4d\gamma_5$
			260	38.5	170	—	—	$^2\Gamma_5\gamma_5^5 \rightarrow {}^2\Gamma\gamma_5^4\gamma_3$?
			230	43.5	(500)	—	—	?
		$Ru(NH_3)_5Br^{2+}$ [87]	398	25.1	1,920	—	—	$\pi Br \rightarrow 4d\gamma_5$
			330	30.3	400	—	—	?
		$Ru(CN)_6^{3-}$ [43]	460	21.8	3,000	—	—	$\pi CN \rightarrow 4d\gamma_5$
			355	28.2	5,000	—	—	?

TABLE VIII (Continued)

			λ	σ	ε	δ	$P \cdot 10^{-5}$	
$4d^6$	Rh(III)	$Rh(H_2O)_6^{3+}$ [58,115]	394	25.4	70	2.4	160	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
			305	32.8	65	—	150	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
		$RhCl_6^{3-}$ [115,137]	(680)	(14.7)	3	1.2	3	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4\gamma_5^5\gamma_3$
			518	19.3	102	1.5	140	$\rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
			412	24.3	82	1.6	130	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
			255	39.2	30,000	2.8	80,000	odd $\pi\gamma_4 \rightarrow 4d\gamma_3$
		$RhBr_6^{3-}$ [115,137]	553	18.1	190	1.5	250	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
			(450)	(22.2)	180	—	250	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
			332	30.1	9,800	2.2	20,000	odd $\pi(a\gamma_8) \rightarrow 4d\gamma_3$
			294.5	33.9	15,300	—	30,000	odd $\pi(b\gamma_8) \rightarrow 4d\gamma_3$
		Rh ox_3^{3-} [115]	(520)	(19.2)	8	1.0	10	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4\gamma_5^5\gamma_3$
			398	25.1	290	2.0	540	$\rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
			(333)	(30.0)	—	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
			(280)	~(36)	(2,000)	—	—	internal oxalate
		$Rh(NH_3)_6^{3+}$ [115]	306	32.7	135	2.3	300	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
			256	39.1	100	2.7	250	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
		$Rh(NH_3)_5Cl^{2+}$ [115]	349	28.7	100	2.0	210	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
			277	36.1	103	2.8	270	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
			~188	~53	(20,000)	—	—	$\sigma Cl \rightarrow 4d\gamma_3$
		$Rh(NH_3)_5Br^{2+}$ [115,130]	424	23.6	25	1.1	30	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4\gamma_5^5\gamma_3$
			359	27.8	122	2.0	260	$\rightarrow {}^1\Gamma_4(t5)\gamma_5^5\gamma_3$
			246	40.6	950	—	—	$\pi Br \rightarrow 4d\gamma_3$
			~200	~50	15,000	—	—	$\sigma Br \rightarrow 4d\gamma_3$
		$Rh(NH_3)_5I^{2+}$ [115,125]	416	24.1	270	2.1	—	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4, {}^1\Gamma_4$
			(388)	(25.8)	230	—	—	$\rightarrow {}^3\Gamma_4, {}^1\Gamma_4$
			278	36.0	3,200	2.5	7,400	$\pi I \rightarrow 4d\gamma_3$
			226	44.3	20,000	2.3	40,000	$\sigma I \rightarrow 4d\gamma_3$

$Rh(NH_3)_5H_2O^{3+}$ [115]	316	31.6	105	2.8	260	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	263	38.1	89	2.8	230	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
$Rh\ en_3^{3+}$ [115]	301	33.2	210	2.4	480	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	253	39.6	190	—	460	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
cis-$Rh\ en_2Cl_2^+$ [1a]	352	28.4	155	—	—	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	295	33.9	180	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
trans-$Rh\ en_2Cl_2^+$ [1a]	406	24.6	75	—	—	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4(t5)\gamma_5^5\gamma_3$
	286	35.0	130	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	(237)	(42.2)	1,600	—	—	electron transfer
$RhenCl_4^-$ [1a]	440	22.8	(150)	—	—	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	370	27.0	(175)	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
cis-$Rh\ py_2\ Cl_4^-$ [124]	448	22.4	91	1.8	160	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4(t5)\gamma_5^5\gamma_3$
	~400	~25	weak	—	—	$\rightarrow {}^1\Gamma_4(t2)\gamma_5^5\gamma_3$
	348	28.7	118	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	263.5	38.0	12,000	vibr. $\sigma_c = 0.9$	—	internal py
	222	45.0	36,000	4.8	—	electron transfer?
trans-$Rh\ py_2\ Cl_4^-$ [124]	500	20.0	39	1.6	60	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4(t2)\gamma_5^5\gamma_3$
	431	23.2	92	1.5	130	$\rightarrow {}^1\Gamma_4(t5)\gamma_5^5\gamma_3$
	261	38.3	14,000	vibr. $\sigma_c = 0.9$	—	internal py
	216	46.4	36,000	4.0	—	electron transfer?
cis-$Rh\ ox_2\ Cl_2^{3-}$ [124]	435	23.0	190	1.9	350	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	352	28.4	275	2.5	700	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	285	35.1	1,900	1.9	3,500	internal ox^{2-}
trans-$Rh\ ox_2\ Cl_2^{3-}$ [124]	470	21.3	54	1.5	70	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4(t5)\gamma_5^5\gamma_3$
	398	25.1	38	—	50	$\rightarrow {}^1\Gamma_4(t2)\gamma_5^5\gamma_3$
	285	35.1	1,300	1.8	2,200	internal ox^{2-}
$Rh(S_2P(OC_2H_5)_2)_3$[141]	470	21.3	1,090	2.2	2,200	$^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	410	24.4	780	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	321	31.2	12,600	2.0	22,000	$\pi \rightarrow 4d\gamma_3$
	(273)	(36.6)	(18,000)	—	—	$\sigma \rightarrow 4d\gamma_3$
	258	38.8	23,200	(+) 2.3	(50,000)	

TABLE VIII (Continued)

			λ	σ	ε	δ	$P \cdot 10^{-5}$	
		$Rh(CN)_6^{3-}$ [232]	227	44.1	(500)	2.4	(1,100)	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
			(210)	(47.6)	(440)	—	—	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	Pd(IV)	$PdCl_6^{2-}$ [35,137]	(480)	(20.8)	(700)	1.4	—	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
			340	29.4	14,000	2.6	34,000	odd $\pi\gamma_4 \rightarrow 4d\gamma_3$
			240	41.7	55,000	2.9	145,000	odd $\sigma\gamma_4 \rightarrow 4d\gamma_3$
$4d^8$	Pd(II)	$Pd(H_2O)_4^{2+}$ [130]	379	26.4	86	3.0	250	${}^1\Gamma_{t1} \rightarrow {}^1\Gamma$
		$PdCl_4^{2-}$ [35,130]	(619)	(16.2)	6	—	—	${}^1\Gamma_{t1} \rightarrow {}^3\Gamma$
			474	21.1	166	1.6 (+2.5) irreg.	300	$\begin{cases}(xy) \rightarrow (x^2 - y^2)\\(xz,yz) \rightarrow (x^2 - y^2)\end{cases}$
			(336)	(29.8)	(500)	—	—	$(2z^2 - x^2 - y^2) \rightarrow (x^2 - y^2)$?
			280	35.8	10,500	2.1	20,000	—
			223	44.9	30,000	2.4	70,000	—
		$PdBr_4^{2-}$ [4,130]	505	19.8	330	1.6	450	${}^1\Gamma_{t1} \rightarrow {}^1\Gamma$
			(374)	(26.8)	(3,000)	—	—	—
			332	30.1	(11,000)	1.8	20,000	—
			247	40.5	(30,000)	irreg.	—	—
		PdI_4^{2-} [59,130]	(555)	(18.0)	800	—	—	—
			486	20.6	4,000	broad	—	—
			408	24.6	8,500	1.8	15,000	—
		Pd ox_2^{2-} [130]	383	26.1	120	2.9	350	${}^1\Gamma_{t1} \rightarrow {}^1\Gamma$
		Pd gly_2, aq. [130]	325	30.8	240	2.7	620	${}^1\Gamma_{t1} \rightarrow {}^1\Gamma$
		$Pd(NH_3)_4^{2+}$ [130]	(373)	(26.8)	12	—	—	${}^1\Gamma_{t1} \rightarrow {}^3\Gamma$
			296	33.8	210	2.9	560	$\rightarrow {}^1\Gamma$
		Pd en_2^{2+} [130]	(365)	(27.4)	~10	—	—	${}^1\Gamma_{t1} \rightarrow {}^3\Gamma$
			287.5	34.8	280	2.5	640	$\rightarrow {}^1\Gamma$

		Pd den Cl^{+} 130	335	29.8	480	2.5	1,200	$^1\Gamma_{t1} \to {}^1\Gamma$
		Pd den $(NH_3)^{2+}$ 130	296	33.8	530	3.0	1,400	$^1\Gamma_{t1} \to {}^1\Gamma$
		Pd trien^{2+} 130	296	33.8	800	2.6	2,000	$^1\Gamma_{t1} \to {}^1\Gamma$
		$Pd(CN)_4^{2-}$ 130	240.2	41.6	1,200	0.5	540	internal 4*d*?
			220.5	45.4	7,200	—	(7,000)	—
			212	47.2	9,000	—	—	—
$4d^{10}$	Ag(I)	$Ag(H_2O)_2^{+}$ 251	(224)	44.7	(400)	—	—	$4d\sigma \to 5s\sigma$
			210.5	47.5	900	—	—	$4d\pi(\omega = 3/2) \to 5s\sigma$?
			193	51.9	1,500	—	—	$4d\delta(\omega = 3/2) \to 5s\sigma$?
	Sn(IV)	$SnCl_6^{2-}$ 137	223	44.9	(10,000)	3.1	(30,000)	odd $\pi\gamma_4 \to 5s\gamma_1$
	Sb(V)	$SbCl_6^{-}$ 137,191	271	36.9	(8,000)	2.8	22,000	odd $\pi\gamma_4 \to 5s\gamma_1$
$5s^2$	Sn(II)	$SnCl_4^{2-}$(?) 68,130	(289)	(34.6)	(500)	—	—	$\}\ {}^1\Gamma_1\gamma_1^2 \to {}^3\Gamma_5\gamma_1\gamma_5$
			(264)	(37.9)	2,000	1.6	—	
			222	45.0	21,000	3.2	—	$\to {}^1\Gamma_5\gamma_1\gamma_5$
		$SnBr_4^{2-}$(?) 68	(310)	(32.3)	(2,000)	—	—	$^1\Gamma_1\gamma_1^2 \to {}^3\Gamma_5\gamma_1\gamma_5$
			245	40.9	(20,000)	—	—	$\to {}^1\Gamma_5\gamma_1\gamma_5$
	Sb(III)	$SbCl_4^{-}$(?) 130	(290)	34.5	(300)	—	—	$^1\Gamma_1\gamma_1^2 \to {}^3\Gamma_5\gamma_1\gamma_5$
			231	43.3	~18,000	3.6	60,000	$\to {}^1\Gamma_5\gamma_1\gamma_5$
$5d^0$	W(VI)	WO_4^{2-} 31	199	50.3	—	—	—	$\pi \to 5d\gamma_3$
		WF_6 gas 246	175	57.0	—	vibr.	—	odd $\pi \to 5d\gamma_5$
		WCl_6 137	(447)	(22.4)	~800	—	—	even $\pi\gamma_4 \to 5d\gamma_5$
			379	26.4	~3,000	1.5	—	odd $\pi\gamma_5 \to 5d\gamma_5$
			334	29.9	~8,000	1.6	—	odd $\pi\gamma_4 \to 5d\gamma_5$
	Re(VII)	ReO_4^{-} 6,179	233	43	3,600	vibr. $\sigma_c = 0.7$	—	$\pi\gamma_4 \to 5d\gamma_3$
			~200	~50	6,000	vibr.	—	$\pi\gamma_5 \to 5d\gamma_3$
	Os(VIII)	OsO_4 159	296	33.8	—	vibr. $\sigma_c = 0.8$	—	$\pi\gamma_4 \to 5d\gamma_3$
			247	40.5	—	vibr. $\sigma_c = 0.8$	—	$\pi\gamma_5 \to 5d\gamma_3$
$5d^1$	Re(VI)	ReF_6 gas 138,185	1,960	5.1	—	vibr. irreg.	—	$\Gamma_8(^2\Gamma_5) \to \Gamma_7(^2\Gamma_5)$
			308	32.5	—	irreg.	—	$\to {}^2\Gamma_3$?(ReF_7?)

TABLE VIII (Continued)

			λ	σ	ε	δ	$P \cdot 10^{-5}$	
$5d^2$	Os(VI)	OsF_6 gas [138,185]	2,550	3.9	—	—	—	$\Gamma_3,\Gamma_5(^3\Gamma_4)\gamma_5^2 \rightarrow \Gamma_1(^3\Gamma_4)\gamma_5^2$
			2,330	4.3	—	vibr. irreg.	—	$\rightarrow \Gamma_4(^3\Gamma_4)\gamma_5^2$
			1,180	8.5	—	vibr. irreg.	—	$\rightarrow \Gamma_3,\Gamma_5\gamma_5^2$
			580	17.3	weak	vibr. irreg.	—	$\rightarrow \Gamma_1(^1\Gamma_1)\gamma_5^2$
			~320	~31	—	broad	—	even $\pi\gamma_4 \rightarrow 5d\gamma_5$
			280	35.7	strong	broad	—	odd $\pi\gamma_5 \rightarrow 5d\gamma_5$
			245	40.8	strong	broad	—	odd $\pi\gamma_4 \rightarrow 5d\gamma_5$
		$OsO_2(OH)_4^{2-}$ [168]	680	14.7	(250)	broad	—	$^1\Gamma_{t1}(xy)^2 \rightarrow {}^1\Gamma_{t5}(xy)(xz,yz)$
			340	29.4	(2,500)	—	—	$\pi \rightarrow (xz,yz)$
$5d^3$	Re(IV)	ReF_6^{2-} [48]	926	10.8	—	irreg.	—	$^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3,{}^2\Gamma_4\gamma_5^3$
			875	11.4	—	irreg.	—	
			567	17.65	—	vibr. $\sigma_c = 0.2$	—	$\rightarrow \Gamma_7(^2\Gamma_5)\gamma_5^3$
			503	19.9	—	broad	—	$\rightarrow \Gamma_8(^2\Gamma_5)\gamma_5^3$
			(310)	(32)	—	broad, irreg.	—	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$?
		$ReCl_6^{2-}$ [51a,113,137,216]	1,060	9.4	4.5	vibr. $\sigma_c = 0.16$	—	$^4\Gamma_2\gamma_5^3 \rightarrow {}^2\Gamma_3,{}^2\Gamma_4\gamma_5^3$
			712	14.03	3.4	vibr. $\sigma_c = 0.15$	1	$\rightarrow \Gamma_7(^2\Gamma_5)\gamma_5^3$
			649	15.4	3	irreg.	1.5	$\rightarrow \Gamma_8(^2\Gamma_5)\gamma_5^3$
			(625)	(16.0)	(2)	irreg.		
			(364)	(27.5)	(230)	0.9	200	$\rightarrow {}^4\Gamma_5\gamma_5^2\gamma_3$?
			(320)	(31.3)	2,800	1.1	2,500	even $\pi\gamma_4 \rightarrow 5d\gamma_5$
			(300)	(33.3)	7,000	—	—	—
			281	35.6	12,500	—	12,000	odd $\pi\gamma_5 \rightarrow 5d\gamma_5$
			(256)	(39.1)	7,000	1.0	7,000	$\pi \rightarrow 5d\gamma_5$
		$ReBr_6^{2-}$ [113,137,194,216,225a]	1400	7.1	18	—	—	$^4\Gamma_2\gamma_5^3 \rightarrow \Gamma_8(^2\Gamma_3)\gamma_5^3$
			1100	9.1	24	irreg.	—	$\rightarrow \Gamma_6(^2\Gamma_4)\gamma_5^3$
			755	13.2	13	vibr. $\sigma_c = 0.1$	2	$\rightarrow \Gamma_7(^2\Gamma_5)\gamma_5^3$

		670	14.9	12	irreg.	5	$\rightarrow \Gamma_8(^2\Gamma_5)\gamma_5^3$
		(650)	(15.4)	(9)			
		(490)	(20.4)	180	0.7	110	even $\pi\gamma_4 \rightarrow 5d\gamma_5$
		(437)	(22.9)	1,600	0.6	(900)	—
		(420)	(23.8)	2,300	—	—	—
		(381)	(26.2)	5,200	—	(5,000)	—
		352.5	28.4	9,900	—	(9,000)	—
		325.5	30.8	8,600	—	(7,000)	—
		303	33.0	4,400	—	(3,000)	—
		262.5	38.1	9,700	1.3	(12,000)	—
	ReI_6^{2-} 137,216	860	11.6	(300)	0.35	(100)	—
		696	14.35	(2,400)	0.8	(2,000)	—
		661	15.1	(2,600)	—		
		(599)	(16.7)	(4,800)	—	(5,000)	—
		573	17.45	(5,600)	—		
		(534)	(18.75)	(6,800)	—	(6,000)	—
		517	19.35	(7,800)	—		
		481	20.8	(5,600)	—	(1,000)	—
		(454)	(22.1)	(7,200)	—	(8,000)	—
		444	22.55	(7,800)	—		
		432	23.15	(8,100)	—		
		424	23.6	(7,900)	—		
		387	25.85	(9,200)	—	—	—
Ir(VI)	IrF_6 gas 138,185,217a	1,570	6.4	—	vibr. irreg.	—	$^4\Gamma_2\gamma_5^3 \rightarrow b\Gamma_8\gamma_5^3$
		1,110	9.0	—	vibr. irreg.	—	$\rightarrow c\Gamma_8, \Gamma_6\gamma_5^3$
		795	12.6	weak	vibr. irreg.	—	$\rightarrow \Gamma_7(^2\Gamma_5)\gamma_5^3$
		634	15.8	weak	vibr. irreg.	—	$\rightarrow d\Gamma_8(^2\Gamma_5)\gamma_5^3$
		~330	~30	—	broad	—	even $\pi\gamma_4 \rightarrow 5d\gamma_5$
		282	35.4	strong	broad	—	odd $\pi\gamma_5 \rightarrow 5d\gamma_5$
		238	42.0	strong	broad	—	odd $\pi\gamma_4 \rightarrow 5d\gamma_5$

TABLE VIII (Continued)

			λ	σ	ε	δ	$P \cdot 10^{-5}$	
$5d^4$	Os(IV)	$OsCl_6^{2-}$ 134,137,140b,140c,160	925	10.8	~5	irreg.	—	$a\Gamma_1({}^3\Gamma_4)\gamma_5^4 \rightarrow {}^1\Gamma_3, {}^1\Gamma_5\gamma_5^4$
			855	11.7	~4	irreg.	—	
			580	17.24	9	vibr. $\sigma_e = 0.17$	2	$\rightarrow b\Gamma_1({}^1\Gamma_1)\gamma_5^4$
			418	23.9	1,000	1.0	800	even $\pi\gamma_4 \rightarrow 5d\gamma_5$
			370	27.0	7,300	0.9	6,000	odd $\pi\gamma_5 \rightarrow 5d\gamma_5$
			(341)	(29.3)	7,700	—	(12,000)	odd $\pi\gamma_4 \rightarrow 5d\gamma_5$
			333	30.0	7,900	1.3		
			(301)	(33.2)	1,000	—	(800)	$\gamma_5^4 \rightarrow \gamma_5^3\gamma_3$?
			(278)	(36.0)	700	—	(500)	$\gamma_5^4 \rightarrow \gamma_5^3\gamma_3$?
			255	39.2	2,000	1.4	(2,600)	$\sigma \rightarrow 5d\gamma'_5$?
			213	47.0	25,000	3.5	(80,000)	odd $\pi\gamma_4 \rightarrow 5d\gamma'_3$
		$OsBr_6^{2-}$ 134,137,140b,225a	932	10.7	28	irreg.	—	$a\Gamma_1({}^3\Gamma_4)\gamma_5^4 \rightarrow {}^1\Gamma_3, {}^1\Gamma_5\gamma_5^4$
			882	11.3	28	—	—	
			621	16.1	weak	narrow	—	$\rightarrow b\Gamma_1({}^1\Gamma_1)\gamma_5^4$
			(579)	(17.3)	1,600	1.0	(1,000)	even $\pi\gamma_4 \rightarrow 5d\gamma'_5$
			(528)	(18.95)	3,200	—	(5,000)	odd $\pi\gamma'_7 \rightarrow 5d\gamma_5$
			(506)	(19.75)	4,500	—		
			489.5	20.45	5,600	0.7		
			445	22.6	7,500	0.85	(3,000)	odd $\pi(a\gamma_8) \rightarrow 5d\gamma'_5$
			423	23.7	5,300	—	(1,000)	—
			399	25.05	5,800	1.3	(4,000)	odd $\pi(b\gamma_8) \rightarrow 5d\gamma_5$
			350	28.6	(2,500)	—	—	$\gamma_5^4 \rightarrow \gamma_5^3\gamma_3$?
			280	35.7	10,000	2.6	(20,000)	$\pi(a\gamma'_8) \rightarrow 5d\gamma_3$
			245	40.8	15,000	—	—	$\pi(b\gamma'_8) \rightarrow 5d\gamma_3$
			193	51.9	65,000	3.2	190,000	$\sigma \rightarrow 5d\gamma_3$

		OsI_6^{2-} [137]	(862)	(11.6)	2,500	0.85	(1,500)	even $\pi \rightarrow 5d\gamma_5$?
			813	12.3	4,000	0.45	1,600	odd $\pi\gamma_7 \rightarrow 5d\gamma_5$
			(688)	(14.55)	3,800	0.4	3,000	odd $\pi(a\gamma_8) \rightarrow 5d\gamma_5$
			653	15.3	6,100	0.55		
			550	18.2	4,400	0.4	2,000	odd $\pi(b\gamma_8) \rightarrow 5d\gamma_5$
			537	18.6	4,500	0.6		
			373	26.8	8,000	2.4	18,000	odd $\pi(\gamma_7) \rightarrow 5d\gamma_3$
			333	30.0	7,800	—	15,000	odd $\pi(a\gamma_8) \rightarrow 5d\gamma_3$
			281	35.6	9,200	—	(20,000)	odd $\pi(b\gamma_8) \rightarrow 5d\gamma_3$
			224	44.6	41,000	3.0	115,000	odd $\sigma(c\gamma_8) \rightarrow 5d\gamma_3$
	Pt(VI)	PtF_6 gas [138,185]	3,000	3.3	weak	vibr. irreg.	—	$a\Gamma_1(^3\Gamma_4)\gamma_5^4 \rightarrow \Gamma_4(^3\Gamma_4)\gamma_5^4$
			1,800	5.5	—	vibr. irreg.	—	$\rightarrow a\Gamma_3, a\Gamma_5(^3\Gamma_4)\gamma_5^4$
			835	12.0	—	vibr. irreg.	—	$\rightarrow b\Gamma_3, b\Gamma_5(^1\Gamma_3, {}^1\Gamma_5)\gamma_5^4$
			625	16.0	weak	vibr. irreg.	—	$\rightarrow b\Gamma_1(^1\Gamma_1)\gamma_5^4$
			~500	~20	—	broad	—	even $\pi\gamma_4 \rightarrow 5d\gamma_5$
			~400	~25	strong	broad	—	odd $\pi\gamma_5 \rightarrow 5d\gamma_5$
			307	32.6	strong	vibr. $\sigma_c = 0.55$	—	odd $\pi\gamma_4 \rightarrow 5d\gamma_5$
$5d^5$	Os(III)	$OsCl_6^{3-}$ [137]	(450)	(22)	weak	—	—	$^2\Gamma_5\gamma_5^5 \rightarrow \gamma_5^4\gamma_3$?
			(307)	(32.6)	—	—	—	even $\pi\gamma_4 \rightarrow 5d\gamma_5$
			282	35.45	strong	1.1	—	odd $\pi\gamma_5 \rightarrow 5d\gamma_5$
			262	38.2	strong	—	—	odd $\pi\gamma_4 \rightarrow 5d\gamma_5$
			(254)	(39.4)	—	—	—	
		$OsBr_6^{3-}$ [137]	(465)	(21.5)	(400)	—	—	?
			(390)	(25.6)	(1,400)	—	—	—
			(365)	(27.4)	(2,500)	—	—	—
			355	28.2	(3,200)	0.4	—	—
			347	28.8	(3.200)	—	—	—
			322.5	31.0	(4,000)	0.6	—	—
			(312.5)	(32.0)	(3,600)	—	—	—
			(298)	(33.6)	(4,500)	—	—	—

TABLE VIII (Continued)

			λ	σ	ε	δ	$P \cdot 10^{-5}$	
	Ir(IV)	IrF_6^{2-} [95]	316	31.6	weak	broad	—	$^2\Gamma_5\gamma_5^5 \rightarrow {}^2\Gamma\gamma_5^4\gamma_3$
			213	47.0	strong	broad	—	odd $\pi\gamma_5 \rightarrow 5d\gamma_5$
		$IrCl_6^{2-}$ [116,137]	590	16.95	410	0.8	300	even $\pi\gamma_4 \rightarrow 5d\gamma_5$
			487	20.5	3,280	1.0	2,800	odd $\pi\gamma_5 \rightarrow 5d\gamma_5$
			434	23.05	2,560	—	4,000	odd $\pi\gamma_4 \rightarrow 5d\gamma_5$
			410	24.4	2,410	0.9		
			(360)	(27.8)	300	—	300	$^2\Gamma_5\gamma_5^5 \rightarrow \gamma_5^4\gamma_3$?
			306	32.7	1,180	1.0	1,000	odd $\sigma\gamma_4 \rightarrow 5d\gamma_5$? ?
			232	43.1	21,600	3.4	67,000	odd $\pi\gamma_4 \rightarrow 5d\gamma_3$
		$IrBr_6^{2-}$ [116,137,140b,225a]	(860)	(11.6)	800	0.75	500	even $\pi \rightarrow 5\mathrm{d}\gamma_5$
			(745)	(13.4)	1,570	—	2,400	odd $\pi(\gamma_7) \rightarrow 5d\gamma_5$
			(700)	(14.3)	2,350	—		
			673	14.9	2,520	0.5		
			583	17.15	3,220	0.4	1,300	odd $\pi(a\gamma_8) \rightarrow 5d\gamma_5$
			545	18.35	1,780	—	1,500	odd $\pi(b\gamma_8) \rightarrow 5d\gamma_5$
			509	19.7	1,530	0.8		
			318	31.5	8,000	2.9	20,000	odd $\pi(a\gamma_8) \rightarrow 5d\gamma_3$
			270	37.0	17,000	—	45,000	odd $\pi(b\gamma_8) \rightarrow 5d\gamma_3$
			209	47.9	62,000	2.5	140,000	odd $\sigma(c\gamma_8) \rightarrow 5d\gamma_3$
		Ir py Cl_5^- [124]	625	16.0	400	0.9	300	even $\pi\gamma_4 \rightarrow 5d\gamma_5$
			(503)	(19.9)	2,450	1.3	3,500	odd $\pi\gamma_5 \rightarrow 5d\gamma_5$
			487	20.5	2,600	1.4		
			405	24.7	1,500	1.7	2,500	odd $\pi\gamma_4 \rightarrow 5d\gamma_5$
			(344)	(29.1)	(800)	—	—	$^2\Gamma_5\gamma_5^5 \rightarrow \gamma_5^4\gamma_3$?
			267	37.5	4,900	—	—	internal py
$5d^6$	Ir(III)	$IrCl_6^{3-}$ [115,137]	(615)	(16.3)	7	1.0	7	$^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4\gamma_5^5\gamma_3$

	560	17.9	10	1.2	11	$\rightarrow {}^3\Gamma_4$ or ${}^3\Gamma_5\gamma_5^5\gamma_3$
	415	24.1	76	1.8	125	$\rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	356	28.1	64	2.1	120	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	206	48.5	28,000	4.1	105,000	odd $\pi\gamma_4 \rightarrow 5d\gamma_3$
$IrBr_6^{3-}$ 115,137	597	16.8	27	2.2	40	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4\gamma_5^5\gamma_3$
	447	22.4	230	1.8	350	$\rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	387	25.8	200	1.7	300	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	272	36.8	12,000	2.2	25,000	odd $\pi(a\gamma_8) \rightarrow 5d\gamma_3$
	243	41.1	20,000	—	50,000	odd $\pi(b\gamma_8) \rightarrow 5d\gamma_3$
	209	47.9	62,000	2.5	140,000	odd $\sigma(c\gamma_8) \rightarrow 5d\gamma_3$
$Ir(NH_3)_5Cl^{2+}$ 115	360	27.8	10	1.8	17	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4\gamma_5^5\gamma_3$
	286	35.0	71	3.5	230	$\rightarrow {}^1\Gamma_4(t5)\gamma_5^5\gamma_3$
Ir en_3^{3+} 115	302	33.1	28	2.2	60	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4\gamma_5^5\gamma_3$
	249	40.2	170	2.8	400	$\rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
Ir py Cl_5^{2-} 124	540	18.5	11	1.6	16	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4\gamma_5^5\gamma_3$
	(420)	(23.8)	(100)	2.0	200	$\rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
	329	30.4	2,250	1.8	4,000	$\rightarrow \gamma_5^5(\pi^\star$ py)
	279	35.8	5,100	1.9	9,000	internal py
cis-Ir py_2 Cl_4^- 124	464	21.6	20	2.0	40	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4\gamma_5^5\gamma_3$
	313	32.0	4,700	2.0	9,000	$\rightarrow \gamma_5^5(\pi^\star$ py)
	263	38.0	9,600	vibr. $\sigma_c = 0.8$	—	internal py
trans-Ir py_2 Cl_4^- 124	515	19.4	9	1.6	15	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4(t2)\gamma_5^5\gamma_3$
	(395)	(25.3)	(80)	—	—	$\rightarrow {}^1\Gamma_4(t2)\gamma_5^5\gamma_3$
	316	31.6	4,400	1.5	6,000	$\rightarrow \gamma_5^5(\pi^\star$ py)
	267	37.4	9,300	vibr. $\sigma_c = 0.8$	—	internal py
Ir dip_3^{3+} 177	315	31.8	27,400	—	—	internal dip
	306	32.7	27,600	—	—	internal dip
	280	35.7	(16,400)	broad	—	$5d\gamma_5 \rightarrow \pi^\star$ dip
	257	38.9	36,400	—	—	internal dip

TABLE VIII (Continued)

		λ	σ	ε	δ	$P \cdot 10^{-5}$	
	$Ir(S_2P(OC_2H_5)_2)_3$[141]	472	21.2	230	2.3	500	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4\gamma_5^5\gamma_3$
		381	26.2	1,070	1.9	2,000	$\rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
		(350)	(28.6)	890	—	1,500	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
		267	37.4	12,200	2.2	25,000	$\pi \rightarrow 5d\gamma_3$
		(232)	(43.1)	(19,500)	—	—	$\sigma \rightarrow 5d\gamma_3$?
		219	45.7	23,100	—	—	
Pt(IV)	PtF_6^{2-}[133,208]	(445)	(22.5)	4	—	6	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4\gamma_5^5\gamma_3$
		410	24.4	5	—	10	$\rightarrow {}^3\Gamma_4$ or ${}^3\Gamma_5\gamma_5^5\gamma_3$
		318	31.4	33	2.5	70	$\rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
		275	36.4	24	2.8	60	$\rightarrow {}^1\Gamma_5\gamma_5^5\gamma_3$
	$PtCl_6^{2-}$[116,137,140b]	453	22.1	50	1.9	90	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4\gamma_5^5\gamma_3$
		(353)	(28.3)	490	1.7	700	$\rightarrow {}^1\Gamma_4\gamma_5^5\gamma_3$
		262	38.2	24,500	2.7 (+2.2)	57,000	odd $\pi\gamma_4 \rightarrow 5d\gamma_3$
		202	49.5	53,000	2.5	120,000	odd $\sigma\gamma_4 \rightarrow 5d\gamma_3$
	$PtBr_6^{2-}$[116,137,140b,225a]	(525)	(19.1)	140	—	—	${}^1\Gamma_1\gamma_5^6 \rightarrow {}^3\Gamma_4\gamma_5^5\gamma_3$
		(435)	(23.0)	1,500	—	—	${}^1\Gamma_4$ or even $\pi \rightarrow \gamma_3$
		364	27.5	7,400	2.2	15,000	odd $\pi(a\gamma_8) \rightarrow 5d\gamma_3$
		315	31.8	18,000	1.8	50,000	odd $\pi(b\gamma_8) \rightarrow 5d\gamma_3$
		(300)	(33.3)	(17,000)	1.5		
		226	44.2	70,000	2.0	130,000	odd $\sigma(c\gamma_8) \rightarrow 5d\gamma_3$
		192	52.1	37,000	2.2	76,000	—
	PtI_6^{2-}[116,137]	494	20.25	12,800	1.6	18,000	odd $\pi\gamma_7 \rightarrow 5d\gamma_3$
		(440)	(22.75)	8,300	—	10,000	odd $\pi(a\gamma_8) \rightarrow 5d\gamma_3$?
		343	29.15	17,000	1.7 (+1.2)	22,000	odd $\pi(b\gamma_8) \rightarrow 5d\gamma_3$
		252	39.8	40,000	3.9	150,000	odd $\sigma(c\gamma_8) \rightarrow 5d\gamma_3$
		230	43.5	59,000	narrow	—	odd $\sigma\gamma_6 \rightarrow 5d\gamma_3$?

9	$5d^8$	Pt(II)	$PtCl_4^{2-}$ 34,36,130,146	(550)	(18.2)	6	—	8	${}^1\Gamma_{t1} \rightarrow {}^3\Gamma_{t2}$
				473.5	21.15	15	1.4	20	$\rightarrow {}^3\Gamma_{t5}$
				389	25.7	64	1.7	100	$\rightarrow {}^1\Gamma_{t2}(xy \rightarrow x^2 - y^2)$
				330	30.3	59	—	90	$\rightarrow {}^1\Gamma_{t5}(xz,yz \rightarrow x^2 - y^2)$
				(266)	(37.6)	(300)	—	—	$\rightarrow {}^1\Gamma_{t3}(2z^2 - x^2 - y^2 \rightarrow x^2 - y^2)$
				(232)	(43.1)	6,800	1.4	10,000	?
				216.5	46.1	8,600	—	14,000	?
			$PtBr_4^{2-}$ 5,130,146	(605)	(16.5)	7	1.5	10	${}^1\Gamma_{t1} \rightarrow {}^3\Gamma_{t2}$
				508	19.7	23	—	30	$\rightarrow {}^3\Gamma_{t5}$
				415	24.1	140	1.7	210	$\rightarrow {}^1\Gamma_{t2}(xy \rightarrow x^2 - y^2)$
				(360)	(27.8)	(210)	—	—	$\rightarrow {}^1\Gamma_{t5}(xz,yz \rightarrow x^2 - y^2)$
				268	37.3	6,700	1.8	11,000	?
			PtI_4^{2-} 130	(616)	(16.2)	40	—	—	${}^1\Gamma_{t1} \rightarrow {}^3\Gamma$
				(536?)	(18.6?)	75	—	—	—
				(445)	(22.5)	1,500	—	—	—
				389	25.7	4,400	2.2	9,000	—
				325	30.8	4,100	—	8,000	—
				279	35.8	13,000	2.0	24,000	—
			$Pt(NH_3)_4^{2+}$ 5,34,268	288	34.7	25	2.7	62	${}^1\Gamma_{t1} \rightarrow {}^3\Gamma$
				(244)	(41)	(150)	—	—	$\rightarrow {}^1\Gamma$?
			$Pt(NH_3)Cl_3$ 34,51b	(483)	(20.7)	(5)	1.4	7	${}^1\Gamma_{t1} \rightarrow {}^3\Gamma_{t2}$
				415	24.1	20	2.4	40	$\rightarrow {}^3\Gamma_{t5}$
				346	28.9	110	1.5	150	$\rightarrow {}^1\Gamma_{t2}$
				300	33.3	70	2.1	130	$\rightarrow {}^1\Gamma_{t5}$
				~208	(48)	(8,000)	—	—	—
			Pt en_2^{2+} 268	280	35.8	(30)	—	—	${}^1\Gamma_{t1} \rightarrow {}^3\Gamma$
			$Pt(CN)_4^{2-}$ 130,158	279.9	35.72	1,590	0.48	350	—
				(258.4)	(38.68)	26,000	1.13	35,000	—
				255.2	39.18	29,500	(+0.93)		
				(242)	(41.32)	1,850	—	2,000	—

TABLE VIII (Continued)

			λ	σ	ε	δ	$P \cdot 10^{-5}$	
	Au(III)	$AuCl_4^-$ 71a,130,250	(385 ?)	(26.0 ?)	—	—	—	$^1\Gamma_{t1} \rightarrow {}^3\Gamma$?
			315	31.8	5,100	2.0	10,000	$\pi \rightarrow 5d(x^2 - y^2)$?
			226.5	44.1	34,400	2.0	70,000	$\sigma \rightarrow 5d(x^2 - y^2)$?
		$AuBr_4^-$ 71a,130	(562)	(17.8)	170	0.9	—	—
			(468)	(20.9)	1,000	—	—	—
			380	26.3	4,600	(+2.0)	9,000	—
			254	39.4	24,300	(+1.7)	42,000	—
$5d^{10}$	Au(I)	$Au(CN)_2^-$ 24,130	239.6	41.8	3,300	0.38	1,100	—
			230.3	43.4	3,450	0.8	2,800	—
			211.5	47.4	9,400	0.9	7,700	—
			205.0	48.8	11,100	0.6	6,000	—
	Hg(II)	$HgCl_4^{2-}$ 67,130,181	230.5	43.4	28,000	2.3	60,000	$(\pi,5d\gamma_5) \rightarrow 6s\gamma_1$
		$HgBr_4^{2-}$ 67,181	248	40.4	28,000	2.7	70,000	$(\pi,5d\gamma_5) \rightarrow 6s\gamma_1$
		HgI_4^{2-} 67,181	322.5	31.0	20,000	1.5	30,000	$(\pi,5d\gamma_5) \rightarrow 6s\gamma_1$
	Pb(IV)	$PbCl_6^{2-}$ 92	307	32.6	9,700	—	—	odd $\pi\gamma_4 \rightarrow 6s\gamma_1$
			208	48.1	24,000	—	—	odd $\sigma\gamma_4 \rightarrow 6s\gamma_1$?
$6s^2$	Tl(I)	KCl(6 Cl^-) 106,233	247	40.8	—	—	—	$^1\Gamma_1 \rightarrow {}^3\Gamma_4$(even γ_1)(odd γ_4)
			196	51.0	—	—	—	$\rightarrow {}^1\Gamma_4$(even γ_1)(odd γ_4)
		KI(6 I^-) 269	282	35.5	—	—	—	$^1\Gamma_1 \rightarrow {}^3\Gamma_4$(even γ_1)(odd γ_4)
			233	43.0	—	—	—	$\rightarrow {}^1\Gamma_4$(even γ_1)(odd γ_4)
	Pb(II)	$Pb(H_2O)_x^{2+}$ 66	208.5	48.0	—	—	—	$^1\Gamma_1 \rightarrow {}^3\Gamma 6s6p$
		$PbCl_4^{2-}$(?) 66,181	272	36.8	15,000	1.2	17,000	$^1\Gamma_1 \rightarrow {}^3\Gamma 6s6p$
		KCl(6 Cl^{2-}) 66	273	36.6	(15,000)	—	—	$^1\Gamma_1 \rightarrow {}^3\Gamma_4$(even γ_1)(odd γ_4)
			196	51.0	110,000	—	—	$\rightarrow {}^1\Gamma_4$(even γ_1)(odd γ_1)
		$PbCl(H_2O)_x^+$ 66	227	44.0	12,000	—	—	$^1\Gamma_1 \rightarrow {}^3\Gamma 6s6p$

	PbBr_4^{2-}(?) [181]	302	33.1	(20,000)	0.9	—	$^1\Gamma_1 \rightarrow {}^3\Gamma$
		223	44.9	(80,000)	—	—	$\rightarrow {}^1\Gamma$
	PbI_4^{2-}(?) [181]	362	27.6	—	—	—	$^1\Gamma_1 \rightarrow {}^3\Gamma$
	$\mathrm{Pb(OH)}_4^{2-}$(?) [130]	240	41.7	7,000	2.2	14,000	$^1\Gamma_1 \rightarrow {}^3\Gamma$
	Pb enta^{2-} [130]	242	41.4	10,400	1.6	15,000	$^1\Gamma_1 \rightarrow {}^3\Gamma$
Bi(III)	$\mathrm{Bi(H_2O)}_x^{3+}$ [192]	222	45.1	11,000	—	—	$^1\Gamma_1 \rightarrow {}^3\Gamma$
	BiCl_5^{2-}(?) [192]	327	30.6	16,100	1.0	15,000	$^1\Gamma_1 \rightarrow {}^3\Gamma$
		222.5	44.9	44,000	1.9	70,000	$\rightarrow {}^1\Gamma$
	BiBr_5^{2-}(?) [192]	373	26.8	18,000	0.8	15,000	$^1\Gamma_1 \rightarrow {}^3\Gamma$
		260	38.5	42,000	—	—	$\rightarrow {}^1\Gamma$
	BiI_4^{-}(?) [181]	(450)	(22.2)	(15,000)	(1.3)	(18,000)	$^1\Gamma_1 \rightarrow {}^3\Gamma$
		336	29.8	(35,000)	3.1	(100,000)	$\rightarrow {}^1\Gamma$
	Bi enta^{-} [130]	264	37.9	8,400	1.7	15,000	$^1\Gamma_1 \rightarrow {}^3\Gamma$

The character of electron transfer bands is mainly demonstrated by the decreasing wave numbers in the series chloride, bromide, iodide of a given element, in accordance with Eq. (34). This is of course no completely certain proof, since other M.O. energy differences might vary in the same way. Thus, Chatt, Gamlén, and Orgel[34] point out the presence of the empty, nonbonding $6p_z$ orbital in Pt(II), to which Laporte-allowed transitions could occur from the filled $5d$ subshells. However, at least in the case of the higher oxidation number in $AuCl_4^-$, this explanation is not probable. In general, the empty orbitals above the partly filled shell seem to have very high energy [cf. Fe(II) and Cu(I) transitions] but in most complexes other than in those of Eq. (40) these orbitals are all σ antibonding. Hence, the $5d \rightarrow 6p_z$ cannot be certainly excluded for Pt(II) (and probably occurs ~50,000 cm^{-1} of $Pt(NH_3)_4^{2+}$). If, on the other hand, the bands are caused by electron transfer to the empty d orbital, the central ions seem much more reducing, having a lower value of σ_r in Table VII, than expected, and they are about as reducing as the trivalent ions in hexahalides.

Octahedral complexes, where the symmetry is reduced by the introduction of a halide or an oxide ligand, also have tetragonal symmetry as the square-planar complexes. In low-spin d^5 systems, such as $Ru(NH_3)_5Cl^{2+}$ and $Ru(NH_3)_4Cl_2^+$ studied by Hartmann and Buschbeck[87] and $Ru(H_2O)_5Cl^{2+}$ and $Ru(H_2O)_4Cl_2^+$ studied by Cady and Connick,[29] the electron transfer bands occur at nearly the same place as those of $RuCl_6^{3-}$. On the other hand, in the diamagnetic d^6 systems, such as $Co(NH_3)_5X^{2+}$ and $Rh(NH_3)_5X^{2+}$ (with $X = Cl^-, Br^-, I^-$), the transitions occur at higher wave number than the corresponding hexahalides (extrapolated in the case of Co(III)) because Δ is larger for the ammonia complexes than for hexahalides, i.e., the empty acceptor orbital $2z^2 - x^2 - y^2$ has higher energy. As suggested by Orgel[199] and Yamatera[267] the weak band 8000 cm^{-1} before the strong band is caused by transfer of a π electron from the halogen, while the latter band is caused by the transfer of a σ electron.

We can extrapolate from Table VII that the hypothetical compounds $RuCl_6$ and $OsCl_6$ would have their $\pi \rightarrow \gamma_5$ bands at 6000 and 13,000 cm^{-1}, respectively. According to Fletcher and Woodhead,[56] $RuO_2Cl_4^{2-}$ has its first electron transfer band at 30,000 cm^{-1}, and according to Lott and Symons,[168] $OsO_2Cl_4^{2-}$ has strong bands at 28,600 and 37,000 cm^{-1}. This shift of the bands to much higher wave numbers can be explained by the two d electrons of these (diamagnetic) complexes both concentrating in xy, while the two xz,yz become π antibonding to the two oxygen atoms on the z axis and are the first empty orbitals for electron transfer. The $4d^1$ system $MoOCl_5^{2-}$ has only one of the two possible electrons in the xy orbital, and hence the electron transfer bands[123] at 28,200, 32,200, and 40,700 cm^{-1} are not very different from those expected for $MoCl_6$ (from Table VII, a value of 28,000 cm^{-1} is extrapolated).

It is also rather surprising that *trans*-Cr en_2 $(H_2O)_2^{3+}$ and *trans*-Co en_2 $(H_2O)_2^{3+}$ exhibit about as much tetragonal splitting of the first ligand field band[15,261] as the *trans*-dichlorotetrammine complexes. This can only be interpreted as water having a considerable π bonding, splitting the γ_5 subshell to xz,yz at higher and xy at lower energies. We are here using ammonia and the amines as "standard ligands" since with only one lone-pair they probably represent rather pure examples of σ bonding. Ligands with two or more lone-pairs may then participate in π bonding. We know from the cobalt(III) complexes that π effects in all four halogen ligands are comparable and slightly larger than for water and also similar to nitrogen anions with two lone-pairs (such as N_3^- and RNH^-). We expect the π effects to be roughly twice as large for hydroxide and thrice as large for oxide as for water. We know also that the π effect may become negative, due to the influence of empty π orbitals in the ligands. This is presumably the case in cyanides, Malatesta's ligands CNR, and in arsines R_3As, where the energy of the partly filled subshell γ_5 in octahedral complexes is depressed. If we define a combined σ electrostatic effect σ_X of each ligand X on the partly filled shell of the central atom, and a similar π_X, we can write the energy changes:[266]

$$\begin{array}{lcccc} & xz,yz & xy & x^2-y^2 & 2z^2-x^2-y^2 \\ \mathrm{MX_5Y} & \frac{3}{4}\pi_X+\frac{1}{4}\pi_Y & \pi_X & \sigma_X & \frac{2}{3}\sigma_X+\frac{1}{3}\sigma_Y \\ trans\text{-}\mathrm{MX_4Y_2} & \frac{1}{2}\pi_X+\frac{1}{2}\pi_Y & \pi_X & \sigma_X & \frac{1}{3}\sigma_X+\frac{2}{3}\sigma_Y \\ \mathrm{MX_6} & \pi_X & \pi_X & \sigma_X & \sigma_X \end{array} \tag{41}$$

and the values can be estimated in a typical trivalent ion [such as Co(III)] in units of 1000 cm^{-1}:

	Example	$\Delta = \sigma_X - \pi_X$	σ_X	π_X
C^{2+}	CN^-	32	(24)	(−8)
N^{3+}	NO_2^-	26	(20)	(−6)
N^0	NH_3	22	22	0
N^-	N_3^-	14	24	+10
As^0	R_3As	—	—	−15
O^0	H_2O	17	25	+8
O^-	OH^-	16	32	+16
	oxalate	17	23	+6
O^{2-}	O^{2-}	15	39	+24
S^{4+}	SO_3^{2-}	25	$25 + x$	$-x$
S^-	RS^-	14	$28 + x$	$-x + 14$
F^-	F^-	16	26	+10
Cl^-	Cl^-	14	24	+10
Br^-	Br^-	13	23	+10
I^-	I^-	11	21	+10

(42)

It must be emphasized that a part of Eq. (42) is of fairly speculative nature, as long as we do not have certain important data available. In general, both σ_X and π_X for a given ligand X increase strongly with increasing oxidation number of the central ion (especially π_X becomes less negative for CN^- and R_3As). The corresponding variation of $\Delta = \sigma_X - \pi_X$ is in most cases a mild increase with the oxidation number of the central ion. Equation (41) is verified both by diamagnetic $4d^8$ palladium(II) complexes such as $PdCl_4^{2-}$ having $\pi_{Cl} = 6000$ cm^{-1}, by diamagnetic $4d^6$ complexes[124] such as *trans*-Rh py$_2$ Cl$_4^-$ ($\pi_{Cl} = 7000$ cm^{-1} if $\pi_{py} = 0$) and *trans*-Rh ox$_2$ Cl$_2^{3-}$ (π_{Cl} 8000 cm^{-1} larger than π_{ox}). It may seem surprising that the tetragonal splittings are so small in high-spin, octahedral nickel(II) complexes.[20,117] However, as Schäffer has pointed out, superposition of Gaussian-shaped absorption bands with the same half-width δ gives rise to bands of very nearly Gaussian shape too. If two bands have the same height, their maxima must be separated by at least $1{\cdot}6\delta$ to produce an experimentally significant deviation from a single Gaussian band with only a slightly larger δ. Hence, band splittings below 2000 cm^{-1}

(where there is not at least one narrow component with δ below 1000 cm^{-1}) cannot generally be observed. Further, in the special case of octahedral Ni(II), the excited M.O. configurations $\gamma_5^5\gamma_3^3$ and $\gamma_5^4\gamma_3^4$ both have a triplet term $^3\Gamma_4$ which is roughly equally mixed in the two observed energy levels by a non-diagonal element of interelectronic repulsion equal to $6B$ for $l = 2$. These two configurations happen to have opposite signs of the π-effect contribution, cancelling exactly for 50% mixtures. In the manganese(II) complex Mn py_2 Cl_2, presumably having the microsymmetry *trans*-MnN_2Cl_4, a splitting of $^4\Gamma_4$ of $\gamma_5^4\gamma_3$ is observed[3] corresponding to π_{Cl} approximately 4000 cm^{-1}.

In $OsO_2Cl_4^{2-}$ mentioned above, π_0 is 30,000 cm^{-1} larger than π_{Cl} according to Eq. (41). This is a rather enormous value, but it must be emphasized that this $5d^2$ system is intrinsically Jahn–Teller unstable and may develop similar splittings as the $3d^1$ vanadium(IV) oxo complexes,[123] and which are conspicuous even in the hexaaquo ions $3d^1$ $Ti(H_2O)_6^{3+}$ and $3d^9$ $Cu(H_2O)_6^{2+}$. On the other hand, the π-bonding effects must be rather important in the high oxidation numbers. For instance, the bond-order of each of the four σ bonds in MnO_4^- can hardly be larger than 0.8 [taking into account that manganese(VII) still has a smaller electronegativity than oxygen], which would bring the residual charge on manganese down from $+7$ to $+3.8$. We know that is too positive; a contribution from the π bonds to the empty d shell may bring this number down to $+3$ or $+1.5$. We remember that the energies of typical single bonds, such as H—H or C—C, are 30,000 cm^{-1}. Of course, we cannot use this value to estimate the bond order of π bonds in transition group complexes, since the bond energies have no close connection with the bond numbers (thus the σ bonds in Na_2 or Li_2 are much weaker than in H_2 or even in I_2). Nevertheless, we may assume that while the π bonding has no very strong influence on the bonding energy of hexahalide ions, it must have rather important effects on oxygen complexes of high oxidation numbers. The antibonding character of a given M.O. always gives rise to larger, and sometimes much larger, energy increases than the energy decrease produced by the bonding character of the corresponding lower M.O. For instance, in the hexahalides, the spreading of the group of (nonbonding and bonding) filled π orbitals (as studied in the electron transfer spectra) is half or two-thirds of the shift of the π antibonding part of the partly filled shell (as studied in the ligand field spectra) and estimated in (42). While these effects are dependent on bond energies at the equilibrium internuclear distances of the ground state of the molecule or molecular ion, a rather good impression of antibonding character of the excited orbitals may be obtained from the absorption band half-widths δ, which are proportional to the slope of the potential curves of the excited states. These curves have in most cases minima for larger values of the internuclear distances than existing at the optical excitation from the ground state.[137,198]

Chemically, there is a connection between the position of the electron transfer bands and the stability of a given compound towards decomposition by a redox process. As Professor Jannik Bjerrum said on one occasion, "copper(II) bromide is dark red, and copper(II) iodide is so black that it does not exist at all." However, the chemical reactions may rearrange the internuclear distances to more favorable values than the optical excitation, e.g., the iodine molecules are produced by attempts to make CuI_2. We cannot give a simple answer to the question how low a wave number an electron transfer band may have and the compound still be either thermodynamically stable or at least possible to prepare and isolate. A rather simple argument shows that an electron transfer band at a given wave number is the more "dangerous" the broader it is, since the electron transfer state then is expected to cross the ground state potential curve at only slightly larger internuclear distances. On the other hand, we cannot *a priori* reject the possibility that some complexes normally exist in the "electron transfer" state. Though this is obviously not the case[116] for $IrCl_6^{2-}$, the present author suspects UCl_6 of containing one $5f$ electron and a hole in the π orbitals of the chloride ligands. The first electron transfer band of UF_6 occurs at 27,000 cm^{-1}, and (34) would hence tend to make the wave number negative for UCl_6.

G. Crystalline Compounds

The Pauling electronegativity scale (with F at 4.0 and C at 2.5) has a slope of the function I for $z = 0$ (page 79) approximately

20,000 cm^{-1} per unit. If we concentrate on the values of the ionization energies for neutral gaseous atoms, i.e., $I(\frac{1}{2})$, we obtain a slope of 32,000 cm^{-1} per Pauling unit. Hence, the M.O. energy differences found from electron transfer spectra would suggest a variation of the electronegativity of a metal half a unit or so per unit of oxidation number. However, we are here trying to pour new wine into old bottles. Undoubtedly, the future interest will concentrate on elaborating a set of M.O. energy differences, as McClure[179] suggested: "The next step in making the semi-empirical method more useful is to derive constants from charge transfer spectra similar to the field constants [i.e., Δ] of crystal field theory. These numbers should be characteristic of an ion and its environment, and should be transferable from one system to another. The electronegativity is a somewhat primitive example of one of the kinds of parameters needed." The values of σ_Γ for the central ions and energy differences such as those expressed in Eqs. (34) and (42) undoubtedly satisfy a part of these wishes.

As Mulliken[188] already pointed out in 1932, the most valuable quality of the M.O. theory is that it allows one at the same time to discuss a fractional distribution of charges on the various atoms and to conserve M.O. configurations as a classification of the wave function; the delocalization on different atoms is made already in the orbital and not by a mixing of "ionic" and "covalent" structures in the valency-bond picture. This implies a very great importance of chosing the symmetry, to which the M.O. belong, in an intelligent way. We have discussed above how the principle of microsymmetry was a very valuable inheritance from the more electrostatic branch of ligand field theory. This is equivalent to another principle: that we shall choose our symmetry such that the second-order correlation effects from M.O. configuration intermixing are not larger than the inevitable minimum. Example: the hydrogen molecule H_2 having at its equilibrium internuclear distance a formation energy 38,000 cm^{-1}, relative to two free H atoms, has a correlation energy 9000 cm^{-1} below the lowest single-configuration energy (even $\sigma)^2$ possible, $-29{,}000$ cm^{-1}. Hence, the chemical bonding effects on the two hydrogen atoms are four times larger than the correlation error inherent in the M.O. description, and it is reasonable to talk about linear symmetry with a center of inversion. On the other hand, at very large internuclear distances, the pure M.O. configuration would lead to an energy 52,000 cm^{-1} too large. Hence, it is more physically sound to talk about two 1*s*-systems in spherical symmetry rather than a hydrogen molecule. It is true that the "artificial" M.O. correlation energy at great internuclear distances always can be described by a finite number of M.O. configurations [in our, very special, case, only two are sufficient, (even $\sigma)^2$ and (odd $\sigma)^2$] while an infinite number is necessary for the really serious effects, the 9000 cm^{-1} in the assembled H_2. However, it will be seen that at some distance between the two nuclei, we pass a limit where we are making a greater error in the energy by talking about (even $\sigma)^2$ than by $1s + 1s$. This effect of the two-electron operators, representing the interelectronic repulsion, is something the group-theorists do not dream about; and this is the reason why group-theoretically illegitimate, too high micro-symmetries may sometimes yield better results than the actual, very low, macroscopic symmetries.

A good case is the insufficiency of the energy band method to describe the energy levels of nonmetallic transition group compounds. We must begin by admitting that the energy band method is the logical extension of M.O. theory to consider infinite crystal lattices. In the usual "solid state" textbooks, it is indicated that a sufficient condition for metallic bonding (electric conductance, metallic reflection and high absorption in all the visible range, etc.) is the presence of a partly filled energy band. This is contradicted by usual lanthanide salts, containing a partly filled 4*f* shell, and by two beautiful examples which have recently been studied: manganese(II) oxide and nickel(II) oxide, both crystallized in NaCl lattice. For group-theoretical reasons, the configurations $\gamma_5^3\gamma_3^2$ of each Mn or $\gamma_5^6\gamma_3^2$ of each Ni cannot avoid forming half filled energy bands. Nevertheless, the compounds show the ligand field bands expected for octahedral micro-symmetry,[178,211] and nickel(II) oxide, when pure,[178] is green and isolating while it is black and semi-conducting with traces of Ni(III). The reason for the breakdown of the energy band description is again intimately connected with the interelectronic repulsion. For the naive man, all the γ_3 electrons in NiO have the same energy. It is true that they all need the same energy for being removed; but it is physically obvious that it costs a lot of energy to transfer a γ_3 electron from one nickel atom to another, forming Ni(I) and Ni(III) in the lattice. There is a difference between the electron affinity and the ionization energy of a given atom, roughly the Coulomb integral $J(a\,a)$, which is some 100,000 cm^{-1} in our case. Hence, we do not have a sea of mobile electrons in strongly delocalized orbitals, as in metals, but a fairly ordinary salt with a well-defined electron number close to each atom. The necessary condition for occurrence of metallic bonding must involve some particular need for considerable overlap integrals between the orbitals of various atoms of the metallic element. A closer analysis of the NiO case shows that the actual ground state must be a mixture of infinitely many of the energy band configurations (M.O. belonging to the whole crystal) but separated by non-diagonal elements of interelectronic repulsion from the other energy levels in such a way that a nearly pure micro-symmetry M.O. configuration is valid near to each nickel atom.

A long series of crystals have been studied with approximately octahedral micro-symmetry. Thus, Asmussen and Bostrup[2,20] measured the reflection spectra of the perovskites such as $KNiCl_3$ and $CsNiBr_3$, which all, like anhydrous $NiCl_2$ and $NiBr_2$, have six halides around each nickel atom. $KMnF_3$ and MnF_2 have the same spectrum.[101,244] These entities are not stable in aqueous solution.

Solid materials are often used as host lattices for small admixtures of transition group elements, which then can be studied in an appropriate micro-symmetry. Especially for the study of paramagnetic (electron spin) resonance, needing dilution with diamagnetic materials, and the investigation of fine details of narrow absorption bands at very low temperature, these materials have been very useful. Aluminum oxide with Cr(III), i.e., ruby, and V(III), or magnesium oxide with Fe(II), Co(II), Ni(II) or even trivalent ions such as Cr(III) have recently been much discussed.[157,169,170,171,212,217] The isomorphous series of Tutton salts $(NH_4)_2[M(H_2O)_6](SO_4)_2$ or $K_2[M(H_2O)_6](SO_4)_2$ with M = Mg(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) have always been of great interest to magnetochemists and can also be used as a way to conserve V(II) in air.[132]

In some crystals, it is possible to obtain coordination numbers not known in solution. Thus, Stahl-Brada and Low[240] studied

Co(II) with cubic, 8-coordinated micro-symmetry in CaF_2. Since the ionic radius of Co(II) is smaller than that of Ca(II), the relative influence of the ligands is weakened by the artificially large internuclear distance, and Δ is only -3500 cm^{-1} (values twice the tetrahedral $CoCl_4^{2-}$, $\Delta = -3300$ cm^{-1}, would have been expected) while the nephelauxetic effect is very small, $\beta = 0.98$. On the other hand, it is generally agreed that Cr(III) (having a larger crystallographic radius than Al(III)) is compressed in the ruby and other minerals[190,200,228,229] corresponding to larger values of Δ and smaller values of β.

Tetrahedral nickel(II) is exceedingly rare in solution (excluding salt melts and organic solvents containing dark blue $NiCl_4^{2-}$ and dark green $NiBr_4^{2-}$).[73,79,131] However, in crystals it is fairly easy to obtain. The admixtures in zinc oxide[178] and the blue compounds[227] such as the spinel $NiAl_2O_4$ are good examples. Recently, McClure and Weakliem[180] have studied a series of divalent transition group ions imbedded in zinc oxide and zinc sulfide all showing the spectra expected of tetrahedral micro-symmetry. The nephelauxetic effect is remarkably large in the cobalt(II) sulfide case; $\beta = 0.60$.

It should be possible to study many fluoride complexes of high oxidation number which are not stable in any solvent. Such a case[133] is MnF_6^{2-}, but many other interesting data are lacking, e.g., for $3d^6$ NiF_6^{2-}, $3d^8$ high-spin CuF_6^{3-}, $4d^3$ RuF_6^-, $4d^5$ RhF_6^{2-}, $4d^6$ PdF_6^{2-}, $4d^8$ high-spin, octahedral PdF_2, $5d^3$ OsF_6^-, $5d^4$ OsF_6^{2-} and IrF_6^-, etc.

Many solids present strong colors which are connected with cooperative effects of several metal atoms. Platinum has been partieularly studied.[248] For instance, Magnus' green salt $[Pt(NH_3)_4][PtCl_4]$ (formed from the colorless $Pt(NH_3)_4^{2+}$ and pink $PtCl_4^{2-}$) and the strongly colored and fluorescent salts of the (in solution colorless) ion $Pt(CN)_4^{2-}$ are known to have a sort of one-dimensional, metallic bonding in chains of platinum atoms. Solids involving mixed oxidation numbers often exhibit dramatic color changes. Complex ions containing mixed oxidation numbers are often strongly colored in solution, but have not been very much studied. One example[135] is M. Delépine's green Ir(III, IV, IV) complex $[N\{Ir(SO_4)_2(H_2O)\}_3]^{4-}$. On the other hand, polynuclear complexes with the metal in the same oxidation number do not generally show strong bands in the visible or near ultraviolet, other than those expected of a set of mononuclear entities. This may be compared to the cases of MnO and NiO discussed above. Exceptions are the iron(III) and rhodium(III) hydroxo complexes.[115]

In some solid compounds, it is not easy to draw a distinction between electron transfer spectra and internal transitions in a definite atom. Thus, CuCl, CuBr, and CuI (with tetrahedral micro-symmetry) all show narrow bands near to 25,000 cm^{-1}. Since similar features are not known for the isoelectronic zinc(II) halides, and since no strong shift in wave number is observed between the chloride, bromide, and iodide, an ordinary electron transfer does not seem plausible. Here, the M.O. theory indicates that the first transition will be from the highest filled γ_5 to the lowest, empty orbital γ_1 (seen from the point of view of a copper atom). Since γ_5 is a mixture of $3d$ electrons from Cu and σ and π electrons from the halide in a L.C.A.O. description, and since γ_1 is an antibonding mixture of $4s$ from Cu and σ electrons, we may have any intermediate case between an internal $3d \rightarrow 4s$ in copper and an electron transfer such as $\pi \rightarrow 4s$. In the same way, the strong bands of $HgCl_4^{2-}$ (43,400 cm^{-1}), $HgBr_4^{2-}$ (40,400 cm^{-1}), and HgI_4^{2-} (31,000 cm^{-1})[67,130,181] may already mainly be electron transfer bands, while the bands of $SnCl_6^{2-}$ (44,900 cm^{-1}), $SbCl_6^{-}$ (36,900 cm^{-1}), and $PbCl_6^{2-}$ (32,600 and 48,000 cm^{-1}) most certainly are. At that particular point, silver(I) poses still many unanswered questions. The not very strong bands around 50,000 cm^{-1} of $Ag(H_2O)_2^{+}$ and $Ag(NH_3)_2^{+}$ are presumably mainly $4d \rightarrow 5s$ transitions,[251] while the bands at lower wave numbers of halides in solution and crystals partly seem to have electron transfer character.

Fromherz and his colleagues began in 1927 a study of the halide complexes of the family tin(II), thallium(I), and lead(II),[66,67,68] where the corresponding gaseous ions contain two s electrons. The present author has measured antimony(III), while Hume and Newman[192] studied bismuth(III). This family became interesting to solid state physicists investigating the mixed crystals with alkali halides, and Seitz[233] proposed, 1938, that the weaker band of Tl(I) in such crystals is caused by the atomic transition $^1S_0(6s^2) \rightarrow {}^3P_1(6s6p)$, while the stronger band is caused by

$^1S_0 \rightarrow {}^1P_1$ of the same two configurations. This explanation has been elaborated by many authors.[106,151,258,263] While the mutual distances between the levels $^1S_0$, $^3P_1$, and $^1P_1$ increase considerably with the ionic charge in the isoelectric series Hg,Tl^+,Pb^{2+},Bi^{3+} in gaseous state, the two corresponding absorption bands of the compounds remain nearly at the same place as those of Hg or at even lower wave number. In lead(II) and especially bismuth(III) (see Table VIII), the shift iodide $<$ bromide $<$ chloride $<$ water suggests an electron transfer. As we saw above, M.O. theory is remarkably fit for explaining this evolution, assuming, e.g., in octahedral symmetry the transition $\gamma_1 \rightarrow \gamma_4$ producing $^3\Gamma_4$ and $^1\Gamma_4$ with appropriate delocalization on the central atom and the ligands. Since γ_1 would be σ antibonding to ammonia and water, this may also explain the chemical fact that the s^2-family forms very strong complexes with halides, while amine (and cyanide) complexes are not known. Orgel[201] discusses the rather peculiar stereochemistry of the s^2-family and concludes that similar effects occur as in the hemiedric lone-pairs of nitrogen(III) in NO_2^- and sulfur(IV) in SO_3^{2-} and SO_2 (cf. also Gillespie and Nyholm[74]).

Even the alkali halides present transitions which are intermediate between electron transfer and atomic excitation. Von Hippel[253] explained the two first strong bands by the electrostatic Born-model as transitions, say in NaCl, of $3p$Cl to $3s$ of the nearest and next-nearest Na neighbors. Halide ions in aqueous solution present one (iodide two, due to the intermediate coupling effect separating the states $^2P_{3/2}$ and $^2P_{1/2}$ of the free iodine atom) band which Franck and Scheibe ascribed to electron transfer to one effective acceptor state of the solvent.[213] It is rather intriguing that the wave number differences of the bands of various halides closely follow Eq. (34) both in alkali halide crystals and in aqueous solution. Petersen[209] suggested an analogy with the excited states of the isoelectronic rare gases, e.g., comparing Xe $5p^56s$ with the first excited configuration of I^- in crystals. Recently, Knox and Inchauspé[152] made a group-theoretical investigation of the halogen excitation. Seen from the point of view of a halide ion in NaCl lattice, the highest filled orbital odd γ_4 may produce Laporte-allowed transitions to the empty, even orbitals. The lowest of these is even γ_1, consisting of say $4s$ of the chloride and the linear combination of the six σ ($3s$ Na) orbitals around the chloride. Since 4s(Cl) and 3s(Na) have comparable energies in the lattice, and the unperturbed atomic radial functions are very extended, it is not very easy to predict the relative composition of the M.O. formed. However, there are good arguments for believing that it does not belong to the "conduction energy band," having arbitrarily large values of l close to the atoms. The next empty, even orbital is γ_3, consisting mainly of $\sigma(3s\ \text{Na})$ but $3d$(Cl) may also make a contribution. Experiments[49] show the presence of a rather large number of individual acceptor orbitals in alkali halides below 90,000 cm^{-1}.

The present author believes that the slightly mysterious, single excited state of the solvent surrounding an iodide ion may mainly consist of the spherically symmetric 6s of the iodide itself, following Petersen's suggestion. But in solvents with a larger electron affinity than water, the acceptor orbital may become more and more localized in particular directions in the neighbor molecules. Thus, Kosower[155] studied the ultraviolet bands of alkylpyridinium iodide ion-pairs in various solvents, and he recently found even the 7600 cm^{-1} doublet structure.[156] It is well known that pyridines have low-lying, empty orbitals available, to which γ_5 electrons from iridium(III) may jump[125], as also does α,α'-dipyridyl,[177] of which Williams[259] investigated the "inverted" electron transfer spectra of iron(II) and copper(I) complexes.

H. Lanthanides and 5*f* Elements

The narrow absorption bands caused by internal $4f^n$-transitions in the lanthanides will only be discussed here from a few points of chemical interest. The distribution of the energy levels of a given central ion is mainly a problem of atomic spectroscopy. As shown by Gobrecht and Judd,[126] the value of the electrodynamic Landé parameter ζ_{4f} increases smoothly from 640 cm^{-1} in Ce(III) to 2950 cm^{-1} in Yb(III), having the configurations $4f^1$ and $4f^{13}$, respectively. The interelectronic repulsion parameters, such as E^3, also increase regularly[126,128] from 460 cm^{-1}i n $4f^2$ Pr(III) to 630 cm^{-1} in $4f^{12}$ Tm(III). The individual J levels have been certainly identified (only a few references are given to the very rich literature) in Ce(III),[176] Pr(III),[107] Nd(III),[30,43a,110,219,263]

Tm(III)[40,112] and Yb(III).[119] The more important features in the intermediate lanthanides have been plausibly identified, but much remains to be done.

The nephelauxetic effect is quite conspicuous[53,119] in Pr(III), as discussed on page 70. It becomes less important in the following lanthanides, and is still observable in $4f^7$ Gd(III). As seen from the interelectronic repulsion parameters, $1/\langle r^{-1}\rangle$ shrinks more quickly than the crystallographic ionic radius, and is on average half as large, explaining the very shielded nature of the $4f$ shell.

Recently, it has become quite clear that the actinides have a similar distribution of $5f^n$-levels.[39,136] The Landé parameter ζ_{5f} is at least twice as large as the corresponding ζ_{4f}, and the interelectronic repulsion parameters [especially evident in $5f^2$ U(IV) and $5f^7$ Cm(III)] are about 60% as large as in the lanthanides, indicating a similar decrease in $\langle r^{-1}\rangle$ as when going from $3d$ to $4d$ gaseous ions. The ligand field splittings are larger for $5f$ complexes than for $4f$, but not much larger. The order of magnitude seems to be 1000 and 100 cm^{-1} in the two cases. Rather a long discussion has been made of the octahedral $5f^1$-system NpF_6 where the situation should be particularly simple. In the author's opinion, the narrow bands of this gas at 7300 to 9600 cm^{-1} represent the transition which in spherical symmetry would be ${}^2F_{5/2}$ to ${}^2F_{7/2}$ corresponding to $7/2\zeta_{5f}$, while the broad bands with vibrational structure at 23,000 and 28,000 cm^{-1} are caused by electron transfer from the ligands to the $5f$ shell. Several authors[51,60,75,104] have assigned the latter bands to internal (odd $\gamma_2 \rightarrow$ odd γ_4) $5f$ transitions. Recently, Axe[3a] has shown that the M.O. energy differences between odd γ_2, odd γ_5, and odd γ_4 of $PaCl_6^{2-}$ (Pa(IV) in Cs_2ZrCl_6) are 1500 and 2160 cm^{-1}, respectively, while ζ_{5f} is 1490 cm^{-1}.

A few of the lanthanides exhibit broad, rather intense bands which can be identified with $4f^q \rightarrow 4f^{q-1}5d$ transitions. Freed[61] made this identification in 1931 of the bands at 33,700, 39,600, 41,700, 45,100, and 47,400 cm^{-1} of cerium(III) salts containing $Ce(H_2O)_9^{3+}$. Since gaseous Ce^{3+} has the levels $5d$ at 49,737 and 52,226 cm^{-1} (with the J values 3/2 and 5/2), while Ce(III) anion complexes have the Laporte-allowed $4f \rightarrow 5d$ bands at lower wave numbers[119] than the aquo ion, we have the same evolution as discussed above for the $6s \rightarrow 6p$ bands of lead(II) and bismuth(III), viz. the wave number order gaseous ion > aquo ion > amino-acid complexes > complexes of heavy halides, resembling closely the nephelauxetic series.

Butement[28] found $4f^6 \rightarrow 4f^5 5d$ bands of Sm(II) in the range 17,000–33,000 cm^{-1}, and $4f^7 \rightarrow 4f^6 6d$ of Eu(II) at 31,200 and 40,300 cm^{-1}. Stewart[243] found a band of Tb(III) at 45,600 cm^{-1}, which most probably is caused by $4f^8 \rightarrow 4f^7 5d$. These two facts inform us that the $4f \rightarrow 5d$ transitions have much smaller wave numbers in the divalent than in the trivalent lanthanides; and that only very few trivalent lanthanides, viz., $4f^1$ and $4f^8$, present these bands in the range accessible in aqueous solutions, below 50,000 cm^{-1}. The occurrence in $4f^8$ is a half filled shell phenomenon,[121] the states with maximum value of S making a jump $8D$ (about 50,000 cm^{-1}) by passing $4f^7$ according to Eq. (35). The electron transfer bands of the trivalent lanthanides must have very high wave numbers. A lower limit is set by Eu(III), which according to Eq. (36) has a very strong wave number decrease of the transition $4f^6 \rightarrow \pi^{-1}4f^7$. Actually, an absorption sets in at 47,000 cm^{-1}, suggesting σ_{r} of Eu(III) in Eq. (34) to be 65,000 cm^{-1} (since H_2O has a position close to $\sigma_{\mathrm{r}} - 13{,}000$ cm^{-1}, as seen from the electron transfer bands of[29] $Ru(H_2O)_6^{3+}$ at 44,500 cm^{-1} and $Fe(H_2O)_6^{3+}$ at[150] 42,000 cm^{-1}). On the other hand, the tetravalent lanthanides must have much lower values of σ_{r}. According to a private communication from Dr. Asprey and Dr. Hoppe, the very interesting oxidation numbers $4f^2$ Nd(IV) in Cs_3NdF_7 and $4f^8$ Dy(IV) in Cs_3DyF_7 have electron transfer bands near 26,000 cm^{-1}. The electron transfer spectra of Nd(III), Sm(III), Eu(III), Tm(III) and Yb(III) bromide complexes in ethanol and of sulfur-containing complexes have been interpreted in the theory of optical electronegativities.[140a]

In the actinides, the $5f \rightarrow 6d$ transitions have comparatively smaller wave numbers. Fried and Hindman[63] find nearly the same distribution of bands as of Ce(III) by measuring Pa(IV) in 1M HCl with bands at 36,300, 39,200, and 44,800 cm^{-1}. In uranium(IV) aquo ions, no Laporte-allowed band is observed in the accessible range, while the U(III) ions have $5f^3 \rightarrow 5f^2 6d$ bands at rather low wave numbers,[120] viz., 25,000, 28,600, and 31,200 cm^{-1}. There is some influence of chloro complex formation, comparable to Ce(III) mentioned above.[119] Sjoblom and Hindman[237] found $5f^4 \rightarrow 5f^3 6d$ bands of Np(III) at 34,500, 37,600, and 43,500 cm^{-1}, while they are not observed in Np(IV). Stewart[242] reported similar bands at higher wave numbers in Pu(III) and Am(III). These various data can be summarized in a list as on page 78, viz., the energy difference $5f \rightarrow 6d$ increases 25,000 cm^{-1} for each unit of oxidation number in an isoelectronic series and 7000 cm^{-1} for each new electron with constant oxidation number, i.e., for increasing atomic number Z. Hence, we can only tell at which Z the orbital energies of $5f$ and $6d$ cross if we indicate the oxidation number.

The genuine electron transfer bands of actinide complexes have been rather little studied. There is a small possibility that the bands beginning at 35,000 cm^{-1} of UCl_6^{2-} are $5f^2 \rightarrow 5f6d$, but it is more probable[120] that the excited state is $\pi^{-1}5f^3$. A comparative study of $NpCl_6^{2-}$ and $PuCl_6^{2-}$ in the ultraviolet would be most valuable. If UCl_6^{2-} has the first electron transfer band at 35,000 cm^{-1}, the decrease of σ_r per unit of oxidation number (cf. page 78) is approximately 26,000 cm^{-1} when compared to UF_6 (and assuming that the bands are caused by the same ligand electrons). This difference from the $4d$- and $5d$-hexahalides (15,000 cm^{-1}) may be explained by the more electrostatic character of the actinide complexes. The dioxo ions UO_2^{2+}, NpO_2^{2+}, PuO_2^{2+}, AmO_2^{2+} (having electron transfer bands at much lower wave number than UO_2^+, NpO_2^+, PuO_2^+, and AmO_2^+) are also rather intriguing. The very low intensity of their first bands with vibrational structure (e.g. 24,200 and 31,400 cm^{-1} of[125] UO_2^{2+}) may be caused by small overlap integrals between the appropriate π and $5f$ orbitals rather than Laporte-forbiddenness.

Many chemists have discussed Seaborg's actinide hypothesis[143] and slightly confused two different aspects: whether the chemistry of the actinides resembles that of the lanthanides, and whether the electron configuration of the ground state and the lowest excited states of the complexes really is $5f^q$. Haïssinsky remarks that the elements U, Np, Pu, Am show many more analogies with each other than with the homologous (in electron configuration) rare earths Nd, Pm, Sm, Eu, and he proposed the name uranides for this group.[81] Actually, there is not the slightest logical relation between constant trivalency and the presence of f

electrons in the partly filled shell.[41,136] On the contrary, there is every reason for expecting more varying and higher oxidation numbers among the $5f$ than among the $4f$ elements, comparable to the difference between $3d$ and $4d$ elements, such as iron and ruthenium. The most conspicuous deviation known between the analogies in electron configuration and in chemical properties occurs in helium, which spectroscopically belongs to the alkaline earth group Be, Mg, Ca, Sr, Ba, Ra and not to the other, inert gases. The actinides constitute a similar deviation, in so far goes the clear chemical difference between neodymium and uranium.

III. CONCLUSIONS

In the preceding sections, we have discussed a series of various transitions, being more or less related to n,l-shells of spherical symmetry of the atoms involved. We may want to recapitulate them in a list:

(1) Internal $nd^q \rightarrow nd^q$. These are the "ligand field" transitions so widely studied in all three transition groups.

(2) Internal $nf^q \rightarrow nf^q$ cause the narrow bands of lanthanides and actinides.

(3) $nf^q \rightarrow nf^{q-1}(n+1)d$ as discussed above for Ce(III), Sm(II), Pa(IV), U(III), Np(III).

(4) $ns^2 \rightarrow ns^1np^1$ mixed with electron transfer as discussed for Sn(II), Sb(III), Tl(I), Pb(II), Bi(III).

(5) $nd^q \rightarrow nd^{q-1}(n+1)s$ mixed with "inverted electron transfer" as found in Fe(II), Cu(I), and Ag(I).

(6) $np^6 \rightarrow np^5(n+1)s$ mixed with electron transfer to the metal ions, as found in fairly ionic salts of F^-, Cl^-, Br^-, and I^-, and perhaps also of O^{2-}, S^{2-}, Se^{2-}, and Te^{2-}.

(7) $nd^q \rightarrow \lambda^{-1}nd^{q+1}$ electron transfer bands in the three transition groups. λ^{-1} denotes a hole in the orbitals mainly concentrated on the ligands.

(8) $nf^q \rightarrow \lambda^{-1}nf^{q+1}$ electron transfer bands in the lanthanides and actinides.

(9) $nd^{10} \rightarrow \lambda^{-1}nd^{10}(n+1)s$ electron transfer [cf. group (5)]. Examples Sn(IV), Sb(V), Pb(IV).

(10) $nd^q \rightarrow \lambda^1 nd^{q-1}$ inverted electron transfer from the d shell to an empty orbital λ in the ligands.

Many compounds exhibit, at various wave number ranges, absorption bands from several of the classes given above. It may be remarked that the classes (3), (4), and (6) to (10) comprise Laporte-allowed transitions. In the corresponding wave number range, it will hence not in general be possible to observe the Laporte-forbidden transitions from classes (1), (2), and (5). The list is of course by no means exhaustive; further studies in the vacuo ultraviolet above 50,000 cm^{-1} will undoubtedly reveal other types of transitions. However, only those representing a considerable oscillator strength will clearly be separated from a general background.

Even though the electrostatic model of the energy levels of transition group complexes has shown itself to be unsatisfactory, a very valuable idea remains: the approximation of corresponding *n,l* orbitals in the atoms participating in the chemical bonding. This brings in all our results obtained in atomic spectroscopy as something elucidating the behavior of complexes; and the effects of molecule formation can be qualitatively described on the basis of a linear combination of these atomic orbitals.

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CONVEX MOLECULES IN GASEOUS AND CRYSTALLINE STATES

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I. INTRODUCTION

In 1950 Isihara[1] proved a geometrical identity for convex bodies and pointed out the fact that the identity is useful for treatment of molecular interactions in uniform gases and liquid solutions. His work was improved and generalized by the present author.[2,3]

For spherically symmetric molecules the intermolecular potential is a function of the distance between the molecular centers. The above-mentioned generalization was based on the supposition that the intermolecular potential was a function of the shortest distance between "convex cores" assumed within the molecules. On this supposition a useful expression for the second virial coefficient was obtained; and by virtue of this expression intermolecular potentials between nonspherical molecules were determined. With the use of these intermolecular potentials Koba and the present author[4] calculated lattice constants and cohesive energies in crystalline states.

In 1955 Hadwiger,[5] a mathematician in Switzerland, published a monograph and developed the geometry of convex bodies. He gave a set of three identities, the first identity being the same as Isihara's. It is very interesting that he had independently proved this theorem in the same year, 1950.[6] After a while Hadwiger's second identity was applied to molecular interactions in nonuniform gases.[7] Here molecules were represented by parallel bodies of their convex cores.

The works mentioned were based on molecular models to which the geometry of convex bodies could be applied. Besides these geometrical treatments thermodynamic and transport properties of nonspherical molecules were investigated by Corner,[8] by Pople,[9] by Castle, Jansen and Dawson,[10] by Kihara, Midzuno and Kaneko,[11] by Balescu,[12] and by Curtiss.[13] Corner said in his paper, "I have tried to find an intermolecular potential which satisfies the three conditions of accuracy, generality, and integrability." It is the purpose of the present article to show that the three conditions of accuracy, generality, and integrability are satisfied in a harmonious manner by the convex-core model of intermolecular potential.

In Section II of this article formulas which will be used later are derived in an elementary way; in Section III the convex cores of molecules are determined. Diffusion of heavy molecules is discussed in Section IV with use of the rigid convex model of molecules. The intermolecular potentials for nonspherical molecules are calculated in Section V from the second virial coefficients; their applications to crystalline states are given in Section VI. Section VII treats the role of the electric multipole interactions for convex or quasi-convex molecules in crystals.

II. GEOMETRY OF CONVEX BODIES

A body is called convex if any line segment whose end points are inside lies entirely in that body.

Let us choose a coordinate origin O inside a (fixed) convex body and take coordinates of polar angles θ and φ ($0 \leqq \theta \leqq \pi, 0 \leqq \varphi \leqq 2\pi$). For any θ, φ, there is one and only one plane which is in contact with the convex body and whose normal from the origin is in the direction (θ,φ). This plane is named the supporting plane in the direction (θ,φ); the perpendicular distance from the origin to the supporting plane is called the supporting function when it is considered as a function of θ and φ. The supporting function will be denoted by $H(\theta,\varphi)$. Let us further denote by M the supporting function integrated over all directions,

$$M = \int_0^{2\pi}\int_0^{\pi} H(\theta,\varphi) \sin\theta \, d\theta d\varphi \tag{1}$$

We shall later see that M is the mean curvature integrated over the whole surface of the convex body.

Let us first assume that the convex body has a smooth surface and that each supporting plane has a contact of first order with the convex body. Let $\mathbf{r}(\theta,\varphi)$ be the radius vector from the origin to the contact point of the body with the supporting plane in the direction (θ,φ); compare Fig. 1 (a). Then by use of the unit vector $\mathbf{u}(\theta,\varphi)$ in the direction (θ,φ) we have

$$H(\theta,\varphi) = \mathbf{r}(\theta,\varphi) \cdot \mathbf{u}(\theta,\varphi) \tag{2}$$

and

$$M = \iint \mathbf{r} \cdot \mathbf{u} \sin\theta \, d\theta d\varphi = \iint \mathbf{r} \cdot \left(\frac{\partial \mathbf{u}}{\partial \theta} \times \frac{\partial \mathbf{u}}{\partial \varphi}\right) d\theta d\varphi \tag{3}$$

The surface area S and the volume V of the convex body are given by

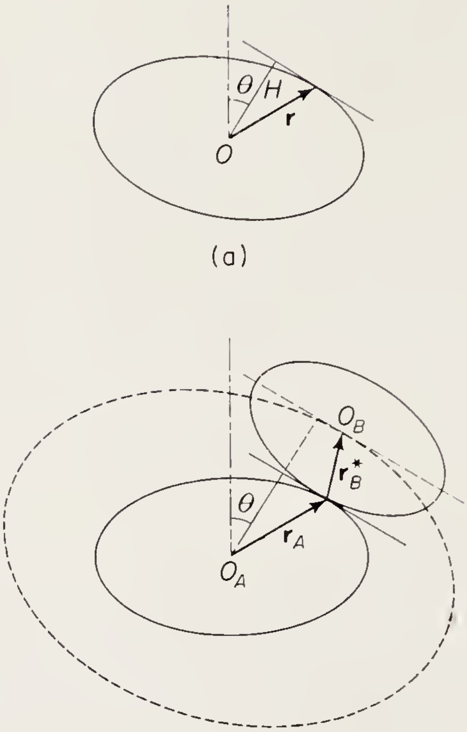
$$S = \iint \left| \frac{\partial \mathbf{r}}{\partial \theta} \times \frac{\partial \mathbf{r}}{\partial \varphi} \right| d\theta d\varphi$$

or, since $(\partial \mathbf{r}/\partial \theta) \times (\partial \mathbf{r}/\partial \varphi)$ is parallel to $\mathbf{u}$,

$$S = \iint \mathbf{u} \cdot \left(\frac{\partial \mathbf{r}}{\partial \theta} \times \frac{\partial \mathbf{r}}{\partial \varphi}\right) d\theta d\varphi \tag{4}$$

and

$$V = \tfrac{1}{3} \iint \mathbf{r} \cdot \left(\frac{\partial \mathbf{r}}{\partial \theta} \times \frac{\partial \mathbf{r}}{\partial \varphi}\right) d\theta d\varphi \tag{5}$$



(a)

(b)

Fig. 1. Convex bodies and their supporting planes.

The quantities V, S, and M are called fundamental measures of a convex body.

As regards a sphere of unit radius we have, from Eq. (3) or Eq. (4),

$$4\pi = \int\int \mathbf{u} \cdot \left(\frac{\partial \mathbf{u}}{\partial \theta} \times \frac{\partial \mathbf{u}}{\partial \varphi} \right) d\theta d\varphi \tag{6}$$

Let A be any convex body; and denote its fundamental measures and $\mathbf{r}$ function by

$$V_A \qquad S_A \qquad M_A \qquad \mathbf{r}(\theta,\varphi)$$

A convex body formed by all points whose distances from the surface of A are smaller than or equal to ρ is called the parallel body of A with the thickness ρ. Let it be denoted by $A + \rho$ (or $\rho + A$). Its $\mathbf{r}$ function is simply given by $\mathbf{r}_A(\theta,\varphi) + \rho\mathbf{u}(\theta,\varphi)$.

The fundamental measures of the parallel body $A + \rho$ are calculated to be

$$\begin{aligned} M_{A+\rho} &= \iint (\mathbf{r}_A + \rho\mathbf{u}) \cdot \left(\frac{\partial \mathbf{u}}{\partial \theta} \times \frac{\partial \mathbf{u}}{\partial \varphi}\right) d\theta d\varphi \\ &= M_A + 4\pi\rho \end{aligned} \tag{7}$$

$$\begin{aligned} S_{A+\rho} &= \iint \mathbf{u} \cdot \left[\frac{\partial(\mathbf{r}_A + \rho\mathbf{u})}{\partial \theta} \times \frac{\partial(\mathbf{r}_A + \rho\mathbf{u})}{\partial \varphi}\right] d\theta d\varphi \\ &= S_A + 2M_A\rho + 4\pi\rho^2 \end{aligned} \tag{8}$$

$$\begin{aligned} V_{A+\rho} &= V_A + \int_0^\rho S_{A+\rho} d\rho \\ &= V_A + S_A\rho + M_A\rho^2 + (4\pi/3)\rho^3 \end{aligned} \tag{9}$$

The three relations Eqs. (7), (8), and (9) are called Steiner's formulas.

According to a theorem of Gauss the surface element dS is expressed in the form

$$dS = R_1R_2 \sin \theta \, d\theta d\varphi$$

or

$$\int dS = \iint R_1R_2 \sin \theta \, d\theta d\varphi$$

where R_1 and R_2 are the principal radii of curvature at $\mathbf{r}(\theta,\varphi)$. The surface area of a parallel body with thickness ρ is similarly

$$\begin{aligned} &\iint (R_1 + \rho)(R_2 + \rho) \sin \theta \, d\theta d\varphi \\ &= \iint R_1R_2 \sin \theta \, d\theta d\varphi + \rho \iint (R_1 + R_2) \sin \theta \, d\theta d\varphi + 4\pi\rho^2 \end{aligned}$$

On comparing Eq. (8) we obtain

$$M = \tfrac{1}{2} \iint (R_1 + R_2) \sin \theta \, d\theta d\varphi$$

or, again by use of the Gauss theorem,

$$M = \iint \frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) dS \tag{10}$$

The last relationship indicates that M is the mean curvature integrated over the whole surface of the convex body.

Now we consider two convex bodies labeled A and B and in each body choose a coordinate origin, O_A and O_B. The volume, the surface area, the M value, and the $\mathbf{r}$ function will be denoted by

$$V_A \qquad S_A \qquad M_A \qquad \mathbf{r}_A(\theta,\varphi)$$

and

$$V_B \qquad S_B \qquad M_B \qquad \mathbf{r}_B(\theta,\varphi)$$

respectively. Keeping O_A and the orientation of A fixed, and keeping the orientation of B also fixed, let us move B around A keeping contact on the surface of A. Then the locus of O_B forms the surface of another convex body, named $A + B$, whose $\mathbf{r}$ function is

$$\mathbf{r}_A(\theta,\varphi) + \mathbf{r}_B^\star(\theta,\varphi)$$

with

$$\mathbf{r}_B^\star(\theta,\varphi) \equiv -\mathbf{r}_B(\pi - \theta, \pi + \varphi)$$

as seen in Fig. 1 (b).

The volume of this last convex body $A + B$

$$V_{A+B} = \tfrac{1}{3}\int\!\!\int (\mathbf{r}_A + \mathbf{r}_B^\star) \cdot \left[\left(\frac{\partial \mathbf{r}_A}{\partial \theta} + \frac{\partial \mathbf{r}_B^\star}{d\theta}\right) \times \left(\frac{\partial \mathbf{r}_A}{d\varphi} + \frac{\partial \mathbf{r}_B^\star}{d\varphi}\right)\right] d\theta d\varphi$$

will first be evaluated. Making use of the identity

$$\frac{\partial}{\partial \theta}\left[\mathbf{r}_B^\star \cdot \left(\mathbf{r}_A \times \frac{\partial \mathbf{r}_A}{\partial \varphi}\right)\right] + \frac{\partial}{\partial \varphi}\left[\mathbf{r}_B^\star \cdot \left(\frac{\partial \mathbf{r}_A}{\partial \theta} \times \mathbf{r}_A\right)\right]$$
$$= 2\mathbf{r}_B^\star \cdot \left(\frac{\partial \mathbf{r}_A}{\partial \theta} \times \frac{\partial \mathbf{r}_A}{\partial \varphi}\right) - \mathbf{r}_A \cdot \left(\frac{\partial \mathbf{r}_B^\star}{\partial \theta} \times \frac{\partial \mathbf{r}_A}{\partial \varphi}\right) - \mathbf{r}_A \cdot \left(\frac{\partial \mathbf{r}_A}{\partial \theta} \times \frac{\partial \mathbf{r}_B^\star}{\partial \varphi}\right)$$

we have

$$\int\!\!\int \left[\mathbf{r}_A \cdot \left(\frac{\partial \mathbf{r}_B^\star}{\partial \theta} \times \frac{\partial \mathbf{r}_A}{\partial \varphi}\right) + \mathbf{r}_A \cdot \left(\frac{\partial \mathbf{r}_A}{\partial \theta} \times \frac{\partial \mathbf{r}_B^\star}{\partial \varphi}\right)\right] d\theta d\varphi$$
$$= 2\int\!\!\int \mathbf{r}_B^\star \cdot \left(\frac{\partial \mathbf{r}_A}{\partial \theta} \times \frac{\partial \mathbf{r}_A}{\partial \varphi}\right) d\theta d\varphi$$

since the integral of the derivatives with respect to θ and φ vanishes. Making use of this relation and another similar one, we obtain

$$V_{A+B} = V_A + V_B + \int\int \mathbf{r}_B^\star \cdot \left(\frac{\partial \mathbf{r}_A}{\partial \theta} \times \frac{\partial \mathbf{r}_A}{\partial \varphi}\right) d\theta d\varphi$$
$$+ \int\int \mathbf{r}_A \left(\frac{\partial \mathbf{r}_B^\star}{\partial \theta} \times \frac{\partial \mathbf{r}_B^\star}{\partial \varphi}\right) d\theta d\varphi$$

Up to this point the orientation of the convex body B has been kept fixed. The next step is to take the average with respect to all orientations of the body B. The integrand of the third term on the right can be replaced by

$$\mathbf{r}_B^\star \cdot \mathbf{u}\mathbf{u} \cdot \left(\frac{\partial \mathbf{r}_A}{\partial \theta} \times \frac{\partial \mathbf{r}_A}{\partial \varphi}\right)$$

When $\mathbf{r}_B^\star \cdot \mathbf{u}$ is averaged with respect to the orientation of the body B, the value no longer depends on (θ,φ) and is equal to $(4\pi)^{-1}M_B$. The average value of the third term is therefore $(4\pi)^{-1}M_BS_A$. Thus the average value of V_{A+B} becomes

$$\langle V_{A+B}\rangle_{\mathrm{Av}} = V_A + V_B + (1/4\pi)(M_BS_A + M_AS_B) \tag{11}$$

The surface area of the convex body $A + B$,

$$S_{A+B} = \int\int \mathbf{u} \cdot \left[\left(\frac{\partial \mathbf{r}_A}{\partial \theta} + \frac{\partial \mathbf{r}_B^\star}{\partial \theta}\right) \times \left(\frac{\partial \mathbf{r}_A}{\partial \varphi} + \frac{\partial \mathbf{r}_B^\star}{\partial \varphi}\right)\right] d\theta d\varphi,$$

can be transformed in a similar way into

$$S_{A+B} = S_A + S_B + \int\int \mathbf{r}_B^\star \cdot \left(\frac{\partial \mathbf{r}_A}{\partial \theta} \times \frac{\partial \mathbf{u}}{\partial \varphi}\right) d\theta d\varphi$$
$$+ \int\int \mathbf{r}_B^\star \cdot \left(\frac{\partial \mathbf{u}}{\partial \theta} \times \frac{\partial \mathbf{r}_A}{\partial \varphi}\right) d\theta d\varphi$$

Replacing

$$\mathbf{r}_B^\star \cdot \left(\frac{\partial \mathbf{r}_A}{\partial \theta} \times \frac{\partial \mathbf{u}}{\partial \varphi}\right)$$

by

$$\mathbf{r}_B^\star \cdot \mathbf{u}\mathbf{u} \cdot \left(\frac{\partial \mathbf{r}_A}{\partial \theta} \times \frac{\partial \mathbf{u}}{\partial \varphi}\right)$$

and taking the average with respect to orientation of the convex body B, we obtain

$$\langle S_{A+B}\rangle_{\text{Av}} = S_A + S_B + (1/4\pi)M_B\left[\iint \mathbf{u}\cdot\left(\frac{\partial \mathbf{r}_A}{\partial\theta}\times\frac{\partial \mathbf{u}}{\partial\varphi}\right)d\theta d\varphi \right.$$
$$\left. + \iint \mathbf{u}\cdot\left(\frac{\partial \mathbf{u}}{\partial\theta}\times\frac{\partial \mathbf{r}_A}{\partial\varphi}\right)d\theta d\varphi\right]$$

The [ ]-bracket expression can be reduced to

$$2\iint \mathbf{r}_A\cdot\left(\frac{\partial \mathbf{u}}{\partial\theta}\times\frac{\partial \mathbf{u}}{\partial\varphi}\right)d\theta d\varphi$$

which, by virtue of Eq. (3), is equal to $2M_A$. Hence the result is

$$\langle S_{A+B}\rangle_{\text{Av}} = S_A + S_B + (1/2\pi)M_A M_B \tag{12}$$

The third relation

$$M_{A+B} = \langle M_{A+B}\rangle_{\text{Av}} = M_A + M_B \tag{13}$$

is easy to derive.

After we have obtained these relations it is no longer necessary to assume that the convex body has a smooth surface and that each supporting plane has a contact of first order with the convex body.

Equation (11) was found in 1950 independently by Isihara[1] and Hadwiger;[5] Eqs. (12) and (13) were given by Hadwiger. The elementary proof given above by the present author[3] leans on the work of Minkowski.[14]

Let us next move a convex body B around a convex body A, but keeping it a distance ρ away from A instead of moving it in contact with A's surface. The locus of O_B then forms the surface of a larger convex body denoted by $A + \rho + B$. The convex body is the same as the parallel body of $A + B$ with the thickness ρ, namely $A + \rho + B = (A + B) + \rho$. Hence its fundamental measures are given by the Steiner formulas:

$$\begin{aligned}
V_{A+\rho+B} &= V_{A+B} + \rho S_{A+B} + \rho^2(M_A + M_B) + (4\pi/3)\rho^3 \\
S_{A+\rho+B} &= S_{A+B} + 2\rho(M_A + M_B) + 4\pi\rho^2 \\
M_{A+\rho+B} &= M_A + M_B + 4\pi\rho
\end{aligned}$$

On taking the average with respect to the orientation of B, we finally obtain

$$\begin{aligned}\langle V_{A+\rho+B}\rangle_{\text{Av}} = V_A + V_B &+ (1/4\pi)(M_B S_A + M_A S_B) \\ &+ [S_A + S_B + (1/2\pi)M_A M_B]\rho \\ &+ (M_A + M_B)\rho^2 + (4\pi/3)\rho^3\end{aligned} \tag{14}$$

$$\langle S_{A+\rho+B}\rangle_{\text{Av}} = S_A + S_B + (2\pi)^{-1}M_A M_B + 2(M_A + M_B)\rho + 4\pi\rho^2 \tag{15}$$

$$\langle M_{A+\rho+B}\rangle_{\text{Av}} = M_A + M_B + 4\pi\rho \tag{16}$$

Values of the fundamental measures which we use in this article are the following. For a sphere of radius a

$$V = 4\pi a^3/3 \qquad S = 4\pi a^2 \qquad M = 4\pi a \tag{17}$$

For a regular tetrahedron inscribed in a unit sphere,

$$\begin{aligned}&V = 8\sqrt{3}/27 = 0.51320, \qquad S = 8\sqrt{3}/3 = 4.61880 \\ &M = 2\sqrt{6}\cos^{-1}(-1/3) = 9.36015\end{aligned} \tag{18}$$

For a regular octahedron inscribed in a unit sphere

$$\begin{aligned}&V = 4/3 = 1.33333, \qquad S = 4\sqrt{3} = 6.92820 \\ &M = 6\sqrt{2}\cos^{-1}(1/3) = 10.44504\end{aligned} \tag{19}$$

For a perpendicular cylinder of height l, area of the base f, and circumference of the base c,

$$V = fl \qquad S = 2f + cl \qquad M = \pi l + \tfrac{1}{2}\pi c \tag{20}$$

On taking the limit $l \to 0$, we have

$$V = 0 \qquad S = 2f \qquad M = \tfrac{1}{2}\pi c \tag{21}$$

for a thin plate. On taking, in Eq. (20), the limit $f \to 0$ and $c \to 0$ we have

$$V = 0 \qquad S = 0 \qquad M = \pi l \tag{22}$$

for a thin rod of length l.

III. CONVEX CORES OF MOLECULES

For monatomic molecules the intermolecular potential U is a function of the distance r between molecular centers. For polyatomic molecules we assume a core inside each molecule and suppose that the intermolecular potential U is a function only of the shortest distance ρ between the cores. In order to apply the geometry of convex bodies we further assume that the molecular cores are convex.

To determine the core of a molecule, it is necessary to have information about the interatomic distances (and bond angles if any) within the molecule. This information is collected in Table I. Consulting this table we fix our cores as indicated in

TABLE I. Interatomic Distances*

Molecules		Bonds	Distances, A
Hydrogen	H_2	H—H	0.74
Nitrogen	N_2	N—N	1.094
Oxygen	O_2	O—O	1.10
Fluorine	F_2	F—F	1.44
Chlorine	Cl_2	Cl—Cl	2.01
Carbon dioxide	CO_2	C—O	1.15
Carbon disulfide	CS_2	C—S	1.54
Acetylene	C_2H_2	C—C	1.20
		C—H	1.06
Boron trifluoride	BF_3	B—F	1.30
Boron trichloride	BCl_3	B—Cl	1.74
Ethylene	C_2H_4	C—C	1.33
		C—H	1.087
(Angle H—C—H is $2 \tan^{-1} \sqrt{2} = 109° 30'$)			
Benzene	C_6H_6	C—C	1.397
		C—H	1.085
Methane	CH_4	C—H	1.093
Carbon tetrafluoride	CF_4	C—F	1.36
Carbon tetrachloride	CCl_4	C—Cl	1.755
Silicon tetrafluoride	SiF_4	Si—F	1.54
Silicon tetrachloride	$SiCl_4$	Si—Cl	2.01
Sulfur hexafluoride	SF_6	S—F	1.56

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* The values are chiefly taken from L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948). The value for SF_6 is due to H. Braune and S. Knocke, *Z. physik. Chem. Leipzig* **B21**, 297 (1933).

TABLE II. The Cores of Molecules

Molecules	Cores	V, A^3	S, A^2	M, A
H_2	thin rod joining H	0	0	2.32
N_2	thin rod joining N	0	0	3.44
O_2	thin rod joining O	0	0	3.45
CO_2	thin rod joining O	0	0	7.23
CS_2	thin rod joining S	0	0	9.68
CH_4	tetrahedron joining midpoints of CH	0.084	1.38	5.12
CF_4	tetrahedron joining F	1.29	8.54	12.73
CCl_4	tetrahedron joining Cl	2.77	14.23	16.43
SF_6	octahedron joining F	5.06	16.86	16.29
C_2H_4	thin rod joining C	0	0	4.18
C_6H_6 (benzene)	hexagon joining midpoints of CH	0	19.6	18.3
$C_{10}H_8$ (naphthalene)	octagon joining midpoints of CH	0	44.7	25.8
$C_{14}H_{10}$ (anthracene)	octagon joining midpoints of CH	0	70.1	33.3

Table II. The volume V, the surface area S, and the surface integral of the mean curvature M of the core are also tabulated.

As regards the potential $U(\rho)$, the simplest choice is the rigid-wall model

$$U(\rho) = \begin{cases} \infty & \text{for} \quad \rho < a \\ 0 & \text{for} \quad \rho > a \end{cases}$$

with no attraction. In this case a molecule is represented by a rigid convex body which is a parallel body of the core with thickness a. This model is used in Section IV. In Section V a more refined potential with both attractive and repulsive forces is adopted.

IV. DIFFUSION COEFFICIENT FOR HEAVY MOLECULES

In this section the diffusion coefficient of heavy molecules A in a gas of light spherical (or quasi-spherical) molecules B is treated. It is supposed that a heavy molecule does not greatly change its linear and rotational velocities in a collision with a light molecule. It is further supposed for the present that the concentration of the heavy molecules is very small.

A heavy molecule in a light gas has Brownian motion and the diffusion coefficient D is given by the well-known relation

$$2Dt = \tfrac{1}{3}\,\text{Mean}\,|\mathbf{R}|^2 \tag{23}$$

Here Mean $|\mathbf{R}|^2$ is the mean squared displacement of the heavy molecule in a time interval t, which is taken to be much larger than the period of velocity correlation in the Brownian motion. The displacement $\mathbf{R}$ is given in terms of the velocity $\mathbf{c}_A$ by the relation

$$\mathbf{R} = \int_0^t \mathbf{c}_A(\tau)d\tau$$

and hence

$$\begin{aligned}\frac{1}{t}\,|\mathbf{R}|^2 &= \frac{1}{t}\int_0^t\int_0^t \mathbf{c}_A(\tau)\cdot\mathbf{c}_A(\tau')d\tau' d\tau\\ &= \frac{1}{t}\int_0^t\int_{-\tau}^{t-\tau} \mathbf{c}_A(\tau)\cdot\mathbf{c}_A(\tau+\tau'')d\tau'' d\tau\end{aligned}$$

Since t is much larger than the duration of the velocity correlation, the lower and upper limits of the integration with respect to τ'' can be extended to $-\infty$ and $+\infty$, respectively. Thus

$$\frac{1}{t}\,\text{Mean}\,|\mathbf{R}|^2 = \int_{-\infty}^{\infty} \text{Mean}\,\mathbf{c}_A(0)\cdot\mathbf{c}_A(\tau'')d\tau''$$

and, on changing the integration variable to t,

$$D = \tfrac{1}{3}\int_0^{\infty} \text{Mean}\,\mathbf{c}_A(0)\cdot\mathbf{c}_A(t)dt \tag{24}$$

The velocity $\mathbf{c}_A$ of the heavy molecule is a solution of the Langevin equation

$$m_A(d/dt)\mathbf{c}_A(t) = -K\mathbf{c}_A(t) + \mathbf{F}(t) \tag{25}$$

Here m_A is the mass of the molecule; $-K\mathbf{c}_A$ represents a dynamical friction experienced by the molecule; and $\mathbf{F}$ is the fluctuating part of the force. From this equation follows

$$\begin{aligned}\int_0^\infty \text{Mean } \mathbf{c}_A(0)\cdot\mathbf{c}_A(t)dt \\ &= \int_0^\infty \text{Mean } \mathbf{c}_A(0)\cdot\mathbf{c}_A(0)\exp(-Kt/m_A)dt \\ &= (1/K)m_A \text{ Mean } |\mathbf{c}_A|^2 = (3kT/K)\end{aligned}$$

kT being the Boltzmann constant times the absolute temperature. Hence we have

$$D = kT/K \tag{26}$$

which is known as Einstein's relation.

The dynamical friction acting on a heavy molecule is due to collisions with light gas molecules. It is given by the collision integral

$$-K\mathbf{c}_A = \left\langle \int\int m_B(\mathbf{c}_B - \mathbf{c}'_B)|\mathbf{c}_B - \mathbf{c}_A| d\sigma f(\mathbf{c}_B)\, d\mathbf{c}_B \right\rangle_{\text{Av}} \tag{27}$$

Here m_B is the mass of the light molecule; $\mathbf{c}_B$ and $\mathbf{c}'_B$ are the velocities of the light molecule before and after the collision, respectively; $d\sigma$ is the collision cross section element (surface element perpendicular to the relative velocity $\mathbf{c}_B - \mathbf{c}_A$); $f(\mathbf{c}_B)$ is the Maxwellian velocity distribution function

$$f(\mathbf{c}_B) = n_B(m_B/2\pi kT)^{\frac{3}{2}} \exp(-m_B\mathbf{c}_B^2/2kT)$$

with the number density n_B of the light molecules; and $\langle\ \rangle_{\text{Av}}$ indicates the average value with respect to the orientation of the heavy molecule.

Let us denote by $\mathbf{g}$ and $\mathbf{g}'$ the relative velocities of the light molecule before and after the collision, so that $|\mathbf{c}_B - \mathbf{c}_A| = |\mathbf{g}| = g$. Then, since $m_B \ll m_A$, Eq. (27) can be transformed into

$$-K\mathbf{c}_A = m\left\langle \int\int (\mathbf{g} - \mathbf{g}')g\, d\sigma f(\mathbf{g})[1 - (m\mathbf{g}\cdot\mathbf{c}_A/kT)]d\mathbf{g} \right\rangle_{\text{Av}}$$

where m is the reduced mass and

$$f(\mathbf{g}) = n_B(m/2\pi kT)^{\frac{3}{2}} \exp(-m\mathbf{g}^2/2kT)$$

Denoting by θ the angle of deflection for the relative velocity, $\mathbf{g} \cdot \mathbf{g}' = g^2 \cos \theta$, we obtain

$$-K\mathbf{c}_A = -(m^2/kT) \left\langle \iint \mathbf{g}\mathbf{g} \cdot \mathbf{c}_A (1 - \cos \theta) g \, d\sigma \, f(\mathbf{g}) \, d\mathbf{g} \right\rangle_{\text{Av}}$$

i.e.,

$$K = \tfrac{1}{3}(m^2/kT) \left\langle \iint (1 - \cos \theta) g^3 \, d\sigma \, f(\mathbf{g}) 4\pi g^2 \, dg \right\rangle_{\text{Av}} \qquad (28)$$

The diffusion coefficient is given by the Einstein relation, Eq. (26). It is of the form

$$D = \tfrac{3}{4}(1/n_B)(2\pi kT/m)^{\frac{1}{2}}(1/Q) \qquad (29)$$

in which

$$Q = 2\left\langle \int_0^\infty \int (1 - \cos \theta) d\sigma e^{-\varepsilon} \varepsilon^2 d\varepsilon \right\rangle_{\text{Av}}, \qquad (\varepsilon \equiv mg^2/2kT) \qquad (30)$$

Let us first consider the case in which the heavy molecule is a rigid convex body and the light molecule B is a rigid sphere of radius b. Then the scattering angle θ is independent of the relative velocity, and hence

$$Q = 4\left\langle \int (1 - \cos \theta) d\sigma \right\rangle_{\text{Av}}$$

The center of B is reflected at the surface of a parallel body of the heavy molecule with thickness b (Fig. 2). By assumption, this parallel body does not move during a collision. Let the incident angle (angle between the normal to the surface and the relative velocity) be α; then $1 - \cos \theta$ is equal to $1 + \cos 2\alpha$. Also, since $d\sigma/\cos \alpha$ is the corresponding surface element of the parallel body, the average can be taken with respect to the incident angle, and

$$Q = 4\int dS \, (1/4\pi) \int_0^{\pi/2} (1 + \cos 2\alpha) \cos \alpha \, 2\pi \sin \alpha \, d\alpha = \int dS$$

Hence Q is the surface area of the parallel body of the heavy molecule with thickness b. On representing the heavy molecule itself by a parallel body of its core with thickness a, we have

$$Q = S_A + 2M_A(a + b) + 4\pi(a + b)^2 \qquad (31)$$

where S_A and M_A are fundamental measures of the core.

Observed values of the diffusion coefficient at 0° C and 1 atmosphere are given in Table III. The values which Q must have if D is to satisfy Eq. (29) at that temperature are also listed in that table.

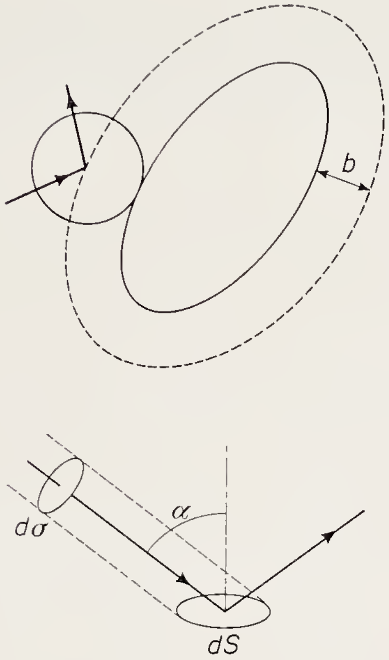

Fig. 2. A light sphere colliding with a heavy convex body.

TABLE III. Diffusion Coefficient D at 0° C, 1 atm., and the Effective Cross-section Q in Eq. (29)

Gases	D, cm^2/sec	Q, A^2
H_2—H_2	1.29	81
H_2—N_2	0.674	114
H_2—O_2	0.697	109
H_2—CO_2	0.550	138
H_2—CS_2	0.369	204
H_2—CCl_4	0.293	255
H_2—SF_6	0.420	178
H_2—C_6H_6	0.318	236
Air–$C_{10}H_8$	0.0513	502
Air–$C_{14}H_{10}$	0.0421	423
N_2—O_2	0.181	150
N_2—CO_2	0.144	176
O_2—CO_2	0.139	175
O_2—CCl_4	0.0636	320
O_2—C_6H_6	0.0797	278
CO_2—CS_2	0.063	316
O_2—O_2	0.187	141
CO_2—CO_2	0.0974	230

Our theory will be applied first to diffusion in hydrogen. The light hydrogen molecule may be approximated by a sphere; its radius *b* is then determined to be 1.27 A from the observed coefficient of self diffusion. Equation (31) enables us to determine the value of *a*, the thickness of the parallel body representing a heavier molecule in hydrogen. Results for nitrogen, N_2, oxygen, O_2, carbon dioxide, CO_2, carbon disulfide, CS_2, carbon tetrachloride,

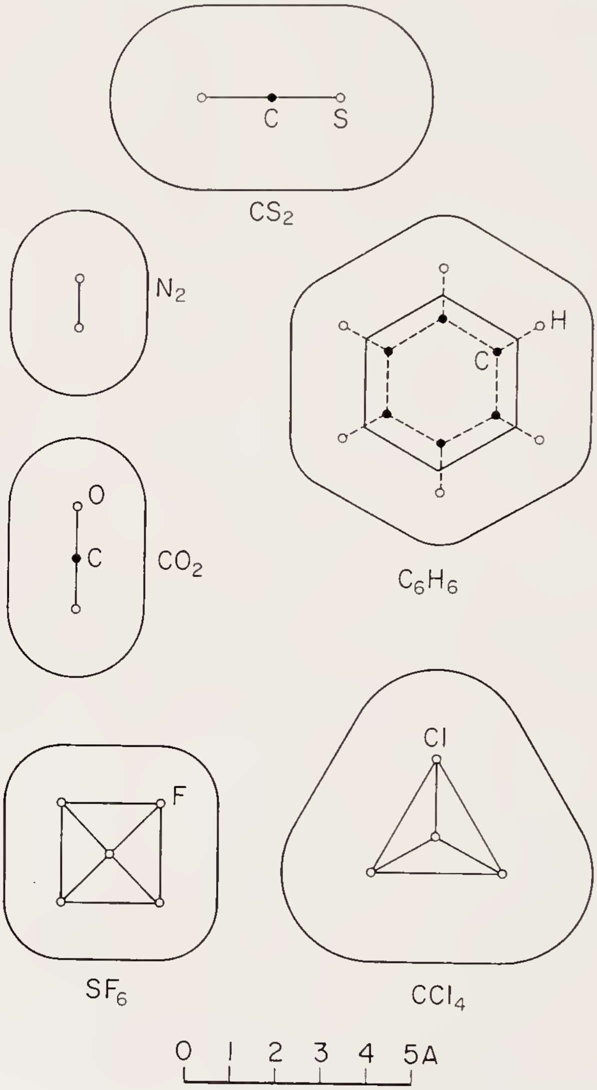

Fig. 3. Shape and size of molecules according to the rigid convex-body model determined from diffusion coefficients at 0°C.

CCl_4, sulfur hexafluoride, SF_6, and benzene, C_6H_6, are given in Table IV. The parallel body with the thickness a represents the shape and size of each molecule as shown in Fig. 3. Its surface area S_{A+a} and mean-curvature integral M_{A+a} are also given in Table IV.

We can treat in the same way the diffusion of naphthalene, $C_{10}H_8$, and anthracene, $C_{14}H_{10}$, in air, which is a light gas in comparison with such heavy molecules. The radius b of the sphere representing an "air molecule" is determined from the coefficient of diffusion at 0° C to be 1.73 A. Results are included in Table IV.

TABLE IV. Constants of Rigid Convex Body Model of Molecules Determined from Coefficients of Diffusion at 0° C

Molecules	a, A	S_{A+a}, A^2	M_{A+a}, A
N_2	1.48	37.7	22.0
O_2	1.41	34.7	21.2
CO_2	1.50	50.0	26.1
CS_2	2.06	92.9	35.5
CCl_4	1.99	129	41.5
SF_6	1.24	76.6	31.9
C_6H_6	1.68	116	39.3
$C_{10}H_8$	2.08	206	51.8
$C_{14}H_{10}$	2.06	260	59.1

We have tacitly assumed that the velocity distribution for the light molecules was Maxwellian. This is in fact true when the frequency of collisions between heavy and light molecules is much smaller than that between light molecules. In this case our expressions are exact. The coefficient of diffusion for the gaseous mixture A and B in general cannot be written exactly in closed form, but it is well approximated by the expression

$$D = \frac{3}{4(n_A + n_B)} \left(\frac{2\pi kT(m_A + m_B)}{m_A m_B}\right)^{\frac{1}{2}} \frac{1}{Q} \tag{32}$$

Here m_A and n_A are the molecular mass and the number density of the species A; m_B and n_B are those of the species B; and Q is an effective surface area for collisions between species A and B. If the molecules of both species are rigid convex bodies, Q is independent of the temperature.

Collisions between two convex bodies in general, however, constitute a difficult dynamical problem; two colliding convex bodies rotate in a complicated manner, making several contacts in general. To this formidable problem a geometrical approach is suggested by the present author which is based on the assumption that the effect of molecular rotation vanishes in the average. In this approximation Q is given by Eq. (15):

$$Q = S_A + S_B + (2\pi)^{-1}M_AM_B + 2(M_A + M_B)(a + b) + 4\pi(a + b)^2 \tag{33}$$

Here S_A and M_A are fundamental measures of the core A, and a is the thickness of the parallel body which represents the molecule A; S_B, M_B, and b are those for B. In Table V calculated values on the right column are compared with observed values on the center column. There is agreement within experimental accuracy indicating that our approximation is close to reality.

TABLE V. Comparison between Q in Table III and its Geometrical Approximation, Eq. (33)

Pairs of Molecules	Q_{obs}, A^2	Q_{calc}, A^2
N_2—O_2	15°	147
N_2—CO_2	176	179
O_2—CO_2	175	173
O_2—CCl_4	320	304
O_2—C_6H_6	278	283
CO_2—CS_2	316	292
O_2—O_2	141	141
CO_2—CO_2	230	208

V. SECOND VIRIAL COEFFICIENTS FOR CONVEX MOLECULES

The equation of state of gases can be expressed in the form

$$Pv = kT(1 + Bv^{-1} + Cv^{-2} + \cdot\cdot\cdot)$$

where P is the pressure, v is the volume per molecule, and kT is the Boltzmann constant times the absolute temperature. In this expression B is called the second virial coefficient and is a function of the temperature. (The notation B for the second virial coefficient should not be confused with the molecular species B.) The term Bv^{-1} is due to interaction between two molecules.

The second virial coefficient B for a single-component gas is given by

$$B = \frac{1}{2}\left\langle \int \left(1 - \exp \frac{-U}{kT}\right) d\tau \right\rangle_{\text{Av}}$$

Here $d\tau$ is the volume element occupied by the center of the one molecule with respect to the other; $\langle\ \rangle_{\text{Av}}$ indicates the average value regarding the molecular orientation. For spherically symmetric molecules with the intermolecular potential $U(r)$, in particular, we have

$$B = \frac{1}{2}\int_0^\infty \left[1 - \exp \frac{-U(r)}{kT}\right] 4\pi r^2 dr \tag{34}$$

Here $4\pi r^2$ is the surface area of a sphere formed by moving the one molecule around the other at a distance r between the centers.

Our convex-core model of molecules is defined on the assumption that the intermolecular potential U is a function of only the shortest distance ρ between the cores. Hence, while it may introduce the principal notion of a nonspherical interaction, the dependence of the potential depth on the molecular orientation is not taken into consideration.

For this model of molecules the second virial coefficient is expressed in the form

$$2B = \int_0^\infty \left[1 - \exp \frac{-U(\rho)}{kT}\right] \langle S_{\text{core}+\rho+\text{core}}\rangle_{\text{Av}} d\rho + \langle V_{\text{core}+\text{core}}\rangle_{\text{Av}} \tag{35}$$

Here $\langle S_{\text{core}+\rho+\text{core}}\rangle_{\text{Av}}$ is the averaged surface area of a convex body formed by the center of one molecule as it is moved around the other at a distance ρ between the cores. It is given by Eq. (15):

$$\langle S_{\text{core}+\rho+\text{core}}\rangle_{\text{Av}} = 2[S + (4\pi)^{-1}M^2] + 4M\rho + 4\pi\rho^2 \tag{36}$$

where V, S, and M are three fundamental measures of the convex core. Similarly

$$\langle V_{\text{core}+\text{core}}\rangle_{\text{Av}} = 2[V + (4\pi)^{-1}MS] \tag{37}$$

Assuming that

$$U(r) = \frac{\lambda}{r^n} - \frac{\mu}{r^m} = U_0 \left[\frac{m}{n-m} \left(\frac{r_0}{r} \right)^n - \frac{n}{n-m} \left(\frac{r_0}{r} \right)^m \right]$$

$$\lambda,\mu > 0, \qquad n > m > 3$$

Lennard-Jones evaluated Eq. (34) in the form of a power series. On integrating by parts, he first obtained

$$B = -\frac{2\pi}{3} \int_0^\infty \frac{1}{kT} \frac{dU(r)}{dr} \exp \frac{-U(r)}{kT} r^3 dr$$

Expanding $\exp(\mu/r^m kT)$ of $\exp[-U(r)/kT]$ into a power series and integrating term by term, he finally obtained

$$B = -\frac{2\pi}{n} \left(\frac{\lambda}{kT} \right)^{3/n} \sum_{t=0}^{\infty} \Gamma \left(\frac{tm-3}{n} \right) \frac{yt}{t!}$$

where $$y \equiv \frac{\mu}{kT} \left(\frac{kT}{\lambda} \right)^{m/n}$$

Following Lennard-Jones we also assume in Eq. (35) that

$$U(\rho) = U_0 \left[\frac{m}{n-m} \left(\frac{\rho_0}{\rho} \right)^n - \frac{n}{n-m} \left(\frac{\rho_0}{\rho} \right)^m \right], \qquad n > m > 3$$

Then we have

$$\begin{aligned} B = {} & (2\pi/3)\rho_0^3 F_3(z) + M\rho_0^2 F_2(z) \\ & + [S + (1/4\pi)M^2]\rho_0 F_1(z) + V + (1/4\pi)MS \end{aligned} \tag{38}$$

where $z = U_0/kT$ and

$$\begin{aligned} F_s(z) &= \int_0^\infty \left[1 - \exp\left(-\frac{m}{n-m} \frac{z}{\xi^n} + \frac{n}{n-m} \frac{z}{\xi^m} \right) \right] d(\xi^s) \\ &= -\frac{s}{n} \sum_{t=0}^{\infty} \frac{1}{t!} \Gamma \left(\frac{tm-s}{n} \right) \left(\frac{n}{m} \right)^t \left(\frac{m}{n-m} z \right)^{[(n-m)t+s]/n} \end{aligned}$$

Two neutral nonpolar molecules at a sufficiently large distance apart attract each other with a potential inversely proportional to the sixth power of the distance. It is reasonable, therefore, to choose $m = 6$. For the case $m = 6$, $n = 12$, in which

$$U(\rho) = U_0[(\rho_0/\rho)^{12} - 2(\rho_0/\rho)^6] \tag{39}$$

calculated values of $F_3(z)$, $F_2(z)$, and $F_1(z)$ are given in Table VI.

TABLE VI[a]

$-\log_{10} z$	$F_3(z)$	$F_2(z)$	$F_1(z)$
−0.4	−9.859	−5.211	−1.784
−0.3	−6.138	−3.008	−0.7761
−0.2	−4.003	−1.776	−0.2221
−0.1	−2.673	−1.027	0.1091
0.0	−1.795	−0.5424	0.3198
0.1	−1.189	−0.2151	0.4600
0.2	−0.7587	0.0132	0.5562
0.3	−0.4465	0.1758	0.6234
0.4	−0.2170	0.2930	0.6710
0.5	−0.0469	0.3779	0.7045
0.6	0.0794	0.4392	0.7279
0.7	0.1729	0.4829	0.7436
0.8	0.2415	0.5134	0.7536
0.9	0.2911	0.5336	0.7591
1.0	0.3259	0.5459	0.7611
1.1	0.3493	0.5521	0.7603
1.2	0.3638	0.5534	0.7575
1.3	0.3715	0.5510	0.7528
1.4	0.3737	0.5457	0.7468
1.5	0.3718	0.5381	0.7396
1.6	0.3668	0.5287	0.7320
1.7	0.3594	0.5179	0.7228
1.8	0.3501	0.5062	0.7135
1.9	0.3396	0.4937	0.7038
2.0	0.3281	0.4806	0.6937

[a] This table is taken from reference 3.

Making use of this table and observed values of the second virial coefficient given in Table VII, we can determine ρ_0 and U_0/k; the results are given in Table VIII. Figure 4 shows the

TABLE VII. The Second Virial Coefficient for Nonspherical Molecules

	T, °K	B, A^3	Reference
H_2	65.1	−30.3	a
	90.0	−9.2	
	123	4.9	
	173	15.1	
	223	20.0	
	273	23.2	
	323	25.1	
	373	25.7	
	473	26.0	
N_2	143	−132	a
	173	−86.0	
	223	−43.8	
	273	−17.2	
	323	−0.4	
	373	10.2	
	423	19.1	
	473	25.5	
	573	34.3	
	673	39.0	
CO_2	273	−241	b
	323	−170	
	373	−119	
	423	−84.0	
	473	−56.6	
	573	−22.5	
	673	−2.6	
	773	10.0	
	873	20.1	
CH_4	273	−89.6	c
	298	−72.1	
	323	−57.6	
	348	−46.1	
	373	−35.9	
	398	−27.2	
	423	−19.3	
CF_4	273	−184	d
	323	−117	
	373	−71.6	
	423	−43.2	
	523	−2.1	
	573	15.4	
	673	38.2	
C_2H_4	273	−280	e
	298	−234	
	323	−197	
	348	−166	
	373	−142	
	398	−121	
	423	−104	
C_6H_6	316	−2160	f
	331	−1890	
	340	−1740	g
	349	−1610	
	363	−1490	
	377	−1380	
	393	−1210	
	409	−1110	h
	424	−950	
	438	−857	

Footnotes to this table on p. 169.

TABLE VIII. Constants in Eq. (39) for the Convex Core Model of Molecules

Molecules	ρ_0, A	U_0/k, °K
H_2	2.81	39.4
N_2	3.47	124
CO_2	3.36	309
CH_4	3.15	226
CF_4	2.55	368
C_2H_4	4.2	256
C_6H_6	3.6	740

parallel body of the core with thickness $\frac{1}{2}\rho_0$, which represents the shape and size of each molecule. It is interesting to note that corresponding molecules shown in Fig. 3 and Fig. 4 are quite similar.

The convex-core model of molecules can also be applied to multicomponent gases. The second virial coefficient B for binary mixtures of species A and B has the form

$$B_{AA}\xi_A^2 + 2B_{AB}\xi_A\xi_B + B_{BB}\xi_B^2 \tag{40}$$

Here ξ_A and $\xi_B \equiv 1 - \xi_A$ are mole fractions of the species A and B, respectively; B_{AA} and B_{BB} are the second virial coefficients

---

Footnotes to Table VII.

[a] The data are due to Holborn and Otto; the values are taken from Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1930), p. 283.

[b] K. E. MacCormack and W. G. Schneider, *J. Chem. Phys.* **18,** 1269 (1950).

[c] A. Michels and G. W. Nederbragt, *Physica* **3,** 569 (1936); see also G. Thomaes and R. Van Steenwinkel, *Nature* **187,** 229 (1960).

[d] K. E. MacCormack and W. G. Schneider, *J. Chem. Phys.* **19,** 845, 849 (1951).

[e] A. Michels and M. Geldermans, *Physica* **9,** 967 (1942).

[f] Francis, McGlasham, Hamann, and McManamey, *J. Chem. Phys* **20,** 1341 (1952).

[g] Andon, Cox, Herington, and Martin, *Trans. Faraday Soc.* **53,** 1074 (1957).

[h] J. D. Cox and R. J. L. Andon, *Trans. Faraday Soc.* **54,** 1622 (1958).

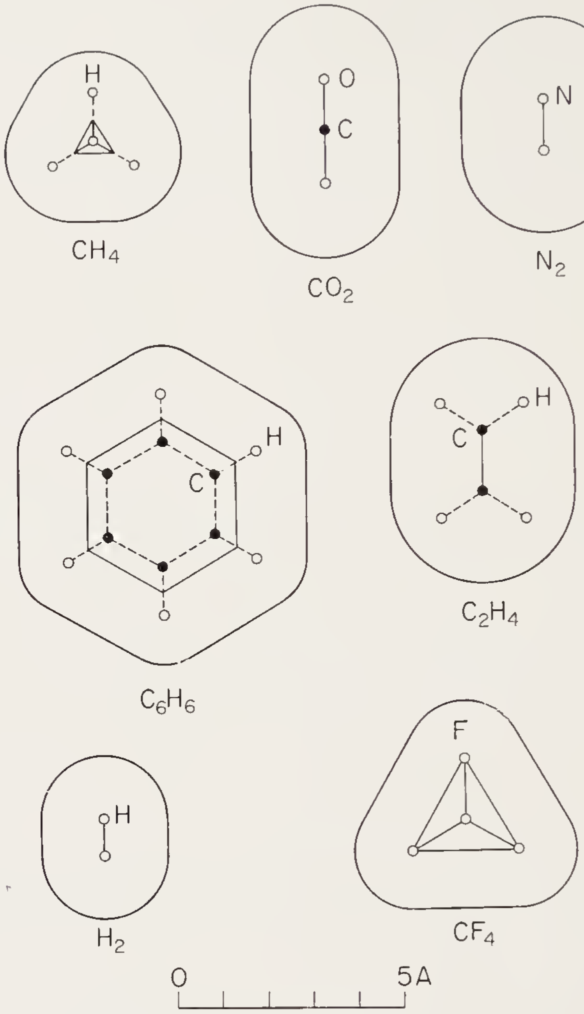

Fig. 4. Shape and size of molecules according to the convex-core model of interactions determined from second virial coefficients.

for pure gases of species A and B. The mixed virial coefficient B_{AB} is given, for our core model of molecules, by

$$2B_{AB} = \int_0^\infty \left[1 - \exp\frac{-U_{AB}(\rho)}{kT}\right] \langle S_{A+\rho+B}\rangle_{\mathrm{Av}} d\rho + \langle V_{A+B}\rangle_{\mathrm{Av}} \quad (41)$$

when the intermolecular potential U_{AB} between A and B is again assumed to be a function of the shortest distance ρ between cores. Here $\langle V_{A+B}\rangle_{\mathrm{Av}}$ and $\langle S_{A+\rho+B}\rangle_{\mathrm{Av}}$ are given by Eqs. (11) and (15).

In particular, when the potential $U_{AB}(\rho)$ is of the Lennard-Jones type,

$$U_{AB}(\rho) = U_{0AB}[(\rho_{0AB}/\rho)^{12} - 2(\rho_{0AB}/\rho)^{6}] \tag{42}$$

we obtain, in terms of $z_{AB} \equiv U_{0AB}/kT$,

$$\begin{aligned} 2B_{AB} = (4\pi/3)\rho_{0AB}^{3}F_{3}(z_{AB}) &+ (M_A + M_B)\rho_{0AB}^{2}F_{2}(z_{AB}) \\ &+ [S_A + S_B + (2\pi)^{-1}M_AM_B]\rho_{0AB}F_1(z_{AB}) \\ &+ V_A + V_B + (4\pi)^{-1}(M_BS_A + M_AS_B) \end{aligned} \tag{43}$$

Here V_A, S_A, M_A are the fundamental measures for the core A, and V_B, S_B, M_B are those for the core B; the functions $F_s(z)$ are the same as in the foregoing discussion.

Regarding the model constants, the relations

$$\begin{aligned} 2\rho_{0AB} &= \rho_{0AA} + \rho_{0BB} \\ U_{0AB}^{2} &= U_{0AA}U_{0BB} \end{aligned} \tag{44}$$

have been verified to hold approximately.[15] Once we have determined the model constants between like molecules, we can calculate, by use of Eq. (44), the mixed second virial coefficient.

VI. CONVEX MOLECULES IN THE CRYSTALLINE STATE

A. Introduction

The cohesive energy and the lattice dimensions of a simple molecular crystal can be calculated and compared with observation by use of the convex-core model of the molecule, when the crystal structure is known. The crystal structure or crystal symmetry itself can not be explained by the core-model interaction only; this problem will be investigated in Section VII. The molecular crystals to be treated here are listed in Tables IX and X.

TABLE IX. Crystal Symmetry

Molecule		System	Lattice	Class
Methane	CH_4	cubic	face-centered	T_d
Carbon dioxide	CO_2	cubic	face-centered	T_h
Nitrogen	N_2	cubic	face-centered	T
Benzene	C_6H_6	orthorhombic	face-centered	D_{2h}
Ethylene	C_2H_4	orthorhombic	body-centered	D_{2h}

TABLE X. Crystal Constants (E = cohesive energy, d = nearest-neighbor distance between lattice points)

Methane	$E = -2.51$ kcal/mol	$d = 4.16$ A
Carbon dioxide	$E = -6.44$ kcal/mol	$d = 4.16$ A
Nitrogen	$E = -1.65$ kcal/mol	$d = 4.00$ A
Benzene	$E = -10.67$ kcal/mol	
	$a = 7.46$, $b = 9.67$, $c = 7.03$ A	at $-3°$ C
	$a = 7.29$, $b = 9.47$, $c = 6.74$ A	at $-195°$ C
Ethylene	$E = -4.5$ kcal/mol	
	$a = 4.87$, $b = 6.46$, $c = 4.14$ A	

The intermolecular potential U is assumed to be in the form of Eq. (39):

$$U(\rho) = U_0[(\rho_0/\rho)^{12} - 2(\rho_0/\rho)^6] \tag{45}$$

where ρ is the intercore distance, U_0 and ρ_0 are constants determined from the second virial coefficient.

B. Methane

The core of a methane molecule CH_4 is defined by a regular tetrahedron connecting the midpoints of CH bonds. The distance of a vertex from the centered carbon atom will be denoted by l, so that $2l = 1.093$ A, the CH-bond length. The parameters in Eq. (45) are

$$\rho_0 = 3.15 \text{ A} \qquad U_0/k = 226° \text{ K}$$

The carbon atoms in a methane crystal occupy the lattice points of a face-centered cubic structure. At temperatures below 20.4° K the molecules do not freely rotate and seem to be parallel to each other with all the CH bonds directed towards the body diagonals. The distance between two nearest-neighbor carbon atoms will be called "nearest-neighbor distance" and denoted by d (so that the lattice constant is $\sqrt{2}d$).

A methane molecule has 12 nearest-neighbor molecules at the intercore distance $d - 2(2/3)^{\frac{1}{2}}l$. In general, the square of the intercore distance, ρ_i^2, between a molecule and its ith neighbor is given in Table XI, where n_i is the number of ith neighbors.

TABLE XI[a]

i	ρ_i^2	n_i
1	$\left(d - 2\sqrt{\frac{2}{3}}\,l\right)^2$	12
2	$\left(\sqrt{2}\,d - \frac{2}{\sqrt{3}}\,l\right)^2$	6
3	$(\sqrt{3}\,d - \sqrt{2}\,l)^2$	24
4	$\left(2d - 2\sqrt{\frac{2}{3}}\,l\right)^2$	12
5	$5d^2 - 8\sqrt{\frac{2}{3}}\,dl + \frac{8}{3}\,l^2$	24

[a] This table is taken from reference 4.

If additivity of potentials is assumed and the zero-point energy is neglected, the cohesive energy per molecule is given by the minimum of

$$\tfrac{1}{2}U_0\sum_{i=1}^{\infty} n_i[(\rho_0/\rho_i)^{12} - 2(\rho_0/\rho_i)^6] \tag{46}$$

as a function of the nearest-neighbor distance d. This expression can be evaluated by the use of Table XI. It takes its minimum

$$-3.29 \text{ kcal/mol} \qquad \text{at} \qquad d = 4.00 \text{ A}$$

The discrepancy between the calculated and observed values (in Table X) may be partly due to the zero-point energy and partly due to nonadditivity of the intermolecular potential. In fact, according to calculations by Kihara and Koba,[4] the zero-point energy is about 0.48 kcal/mol and the effect of nonadditivity is about 0.23 kcal/mol. These two effects slightly increase the nearest-neighbor distance d.

C. Carbon Dioxide

The core of a carbon dioxide molecule CO_2 has the form of a thin rod connecting the two O's, the length l of the rod being $l = 2.30$ A. The potential parameters are

$$\rho_0 = 3.36 \text{ A} \qquad U_0/k = 309^\circ \text{ K}$$

The carbon atoms in a carbon dioxide crystal form a face-centered cubic lattice, which is composed of four simple cubic lattices. On each simple cubic lattice the CO_2 molecules extend in the same direction towards the body diagonals, the direction being different on different simple lattices (cf. Fig. 10). The distance between nearest-neighbor carbon atoms will again be denoted by d.

A carbon atom has 12 nearest carbon neighbors at the distance d; the intercore distance to any of the 12 nearest neighbors is

$$[d^2 - (2/3)^{\frac{1}{2}}dl + (2/9)l^2]^{\frac{1}{2}} \qquad \text{if} \qquad l \leqq (3/2)(3/2)^{\frac{1}{2}}d$$

A carbon atom has 6 second neighbors at the distance $\sqrt{2}d$; the intercore distance to any of the 6 second neighbors is

$$[2d^2 - 2(2/3)^{\frac{1}{2}}dl + l^2]^{\frac{1}{2}} \qquad \text{if} \qquad l \leqq (2/3)^{\frac{1}{2}}d$$

A carbon atom has 24 carbon atoms as third neighbors at the distance $\sqrt{3}d$; the intercore distance to one-half of these is

$$[3d^2 - (6)^{\frac{1}{2}}dl + (2/3)l^2]^{\frac{1}{2}} \qquad \text{if} \qquad l \leqq (3/2)^{\frac{1}{2}}d$$

and that to the others

$$[3d^2 - (2/3)^{\frac{1}{2}}dl + (2/9)l^2]^{\frac{1}{2}} \qquad \text{if} \qquad l \leqq (3/2)(3/2)^{\frac{1}{2}}d$$

In general, when $l \leqq (2/3)^{\frac{1}{2}}d$, we denote by ρ_{ij} the intercore distance to n_{ij} cores of ith neighbors, $\sum_j n_{ij}$ being the total number n_i of the ith neighbors. Values of ρ_{ij}^2 and n_{ij} are given in Table XII.

If additivity is assumed and the zero-point energy is neglected, the cohesive energy per molecule is given by the minimum of

$$\tfrac{1}{2}U_0 \sum_{i,j} n_{ij}[(\rho_0/\rho_{ij})^{12} - 2(\rho_0/\rho_{ij})^6] \tag{47}$$

as a function of the nearest-neighbor distance d. This expression can be evaluated by the use of Table XII. It takes its minimum

$$-4.72 \text{ kcal/mol} \qquad \text{at} \qquad d = 4.19 \text{ A}$$

The discrepancy between the calculated and observed values here cannot be explained by the zero-point energy or by the non-additivity of the potential. In fact, electrostatic interactions are dominant, as shown in the following.

TABLE XII[a]

i	j	ρ_{ij}^2	n_{jj}
1	1	$d^2 - \sqrt{\frac{2}{3}}\,dl + \frac{2}{9}l^2$	12
2	1	$2d^2 - 2\sqrt{\frac{2}{3}}\,dl + l^2$	6
3	1	$3d^2 - \sqrt{6}dl + \frac{2}{3}l^2$	12
3	2	$3d^2 - \sqrt{\frac{2}{3}}\,dl + \frac{2}{9}l^2$	12
4	1	$4d^2 - 4\sqrt{\frac{2}{3}}\,dl + l^2$	6
4	2	$4d^2$	6
5	1	$5d^2 - \sqrt{6}dl + \frac{1}{3}l^2$	12
5	2	$5d^2 - \sqrt{6}dl + \frac{2}{3}l^2$	12
6	1	$6d^2 - 2\sqrt{6}dl + l^2$	2
6	2	$6d^2 - \sqrt{6}dl + \frac{3}{4}l^2$	6
7	1	$7d^2 - 5\sqrt{\frac{2}{3}}\,dl + \frac{2}{3}l^2$	12
7	2	$7d^2 - \sqrt{6}dl + \frac{2}{9}l^2$	12
7	3	$7d^2 - \sqrt{6}dl + \frac{1}{3}l^2$	12
7	4	$7d^2 - \sqrt{\frac{2}{3}}\,dl + \frac{2}{9}l^2$	12
8	1	$8d^2 - 4\sqrt{\frac{2}{3}}\,dl + l^2$	6
9	1	$9d^2 - 5\sqrt{\frac{2}{3}}\,dl + \frac{2}{3}l^2$	12
9	2	$9d^2 - \sqrt{6}dl + \frac{2}{9}l^2$	12
9	3	$9d^2 - \sqrt{6}dl + \frac{2}{3}l^2$	12
10	1	$10d^2 - 2\sqrt{6}dl + l^2$	12
10	2	$10d^2 - 2\sqrt{\frac{2}{3}}\,dl + l^2$	12

[a] This table is taken from reference 4.

The CO_2 molecule has an electric quadrupole

$$Q = \sum_i e_i(z_i^2 - x_i^2) = 3.12 \times 10^{-26} \text{ e.s.u.}$$

where (x_i, y_i, z_i) are coordinates of an electric charge e_i, z_i being in the direction of the molecular axis.

The potential energy between the two quadrupoles at the distance r is given by

$$\tfrac{3}{4}(Q^2/r^5)f(\theta_1,\varphi_1;\ \theta_2,\varphi_2)$$

in which

$$\begin{aligned} f(\theta_1,\varphi_1;\ \theta_2,\varphi_2) \\ &= 1 - 5\cos^2\theta_1 - 5\cos^2\theta_2 - 15\cos^2\theta_1\cos^2\theta_2 \\ &\quad + 2[4\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos(\varphi_1 - \varphi_2)]^2 \end{aligned}$$

Here θ_1, φ_1 are the polar angles of the axis of one quadrupole with respect to the line connecting the two, and θ_2, φ_2 are those of the other. For the CO_2 crystal, the function f is given in Table XIII,

TABLE XIII

Shell no.		Distance from center	Number of molecules	$f(\theta_1,\varphi_1;\ \theta_2,\varphi_2)$
i	j			
1	1	d	12	$-\frac{19}{9}$
2	1	$\sqrt{2}d$	6	$-\frac{28}{9}$
3	1	$\sqrt{3}d$	12	$-\frac{31}{81}$
3	2	$\sqrt{3}d$	12	$+\frac{1}{9}$
4	1	$2d$	6	$+3$
4	2	$2d$	6	$-\frac{13}{9}$

which is due to Jansen, Michels, and Lupton.[16] It is important to note that the sign of f is negative for first and second neighbors.

The contribution of the quadrupole interaction to the cohesive energy is

$$-\tfrac{1}{2} \times 21.4Q^2/d^5 \tag{48}$$

per molecule. The sum of (47) and (48) takes its minimum

$$-5.90 \text{ kcal/mol} \qquad \text{at} \qquad d = 4.16 \text{ A}$$

These values are close to the corresponding observed values.

The small discrepancy between calculated and observed cohesive energies can be eliminated if a somewhat larger core is adopted. (In general, when the core is enlarged, the potential depth U_0 increases and hence the calculated value of the cohesive energy becomes lower.) The most accurate choice will be such as is shown in Fig. 5, the thickness due to the π electrons being taken into account.

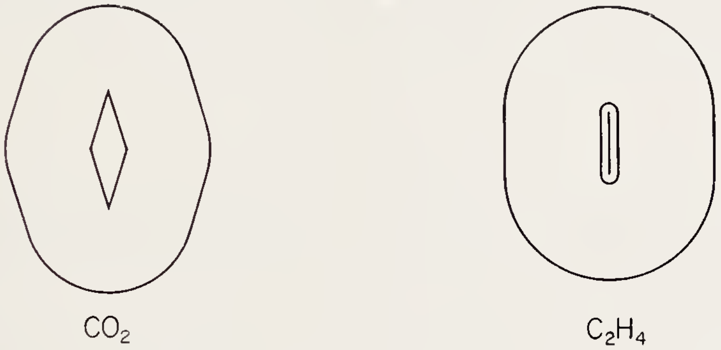

Fig. 5. Models of carbon dioxide and ethylene with thick cores indicating π electrons.

D. Nitrogen

The core of a nitrogen molecule N_2 is a thin rod connecting the two N's, the length of the rod being $l = 1.094$ A. The potential parameters are

$$\rho_0 = 3.47 \text{ A} \qquad U_0/k = 124^\circ \text{ K}$$

Below 35° K nitrogen crystallizes into a cubic structure which is somewhat similar to the structure of carbon dioxide. However, the midpoint of the NN bond is not on the face-centered cubic lattice. It is somewhat shifted along the molecular axis; and the point dividing the bond in the ratio 4 to 7 is on the lattice. This shift cannot be explained by our convex-core model of molecules.

If we neglect the shift, the nonadditivity of the potential and the zero-point energy, we obtain the cohesive energy and the nearest-neighbor distance

$$-1.99 \text{ kcal/mol} \qquad \text{and} \qquad d = 3.83 \text{ A}$$

(A nitrogen molecule has an electric quadrupole $Q = 1.29 \times 10^{-26}$ e.s.u. which contributes -0.30 kcal/mol to the interaction energy. The sum of the zero-point energy and the effect of potential nonadditivity is about 0.6 kcal/mol.)

E. Benzene

As the core of a benzene molecule C_6H_6 we choose a regular hexagon formed by connecting the midpoints of successive CH bonds. (A more accurate shape would be a hexagon plate with nonvanishing thickness.) Since the length of a CC bond in a benzene molecule is 1.397 A, and that of a CH bond is 1.085 A, the length l of one side of the hexagon core is calculated to be

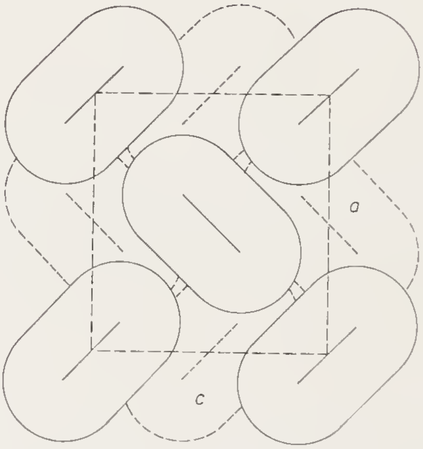

Fig. 6. Face-centered orthorhombic crystal structure of benzene. Cohesive energy and lattice constants are calculated according to this pattern, which is somewhat idealized.

1.940 A. The values of ρ_0 and U_0 determined from the second virial coefficient are

$$\rho_0 = 3.6 \text{ A} \qquad U_0/k = 740° \text{ K}$$

When potential additivity is assumed, and the zero-point energy and the electric multipole interaction are neglected, we obtain −10.2 kcal/mol as the cohesive energy and

$$a = 7.6 \text{ A} \qquad b = 11.0 \text{ A} \qquad c = 6.9 \text{ A}$$

as the lattice constants. These are close to the corresponding observed values (cf. Table X and Fig. 6).

F. Ethylene

As the core of an ethylene molecule C_2H_4 we choose a thin rod connecting two carbon atoms with length $l = 1.33$ A. The choice of a rod core may be reasonable because of the π electrons and because of the fact that each molecule in an ethylene crystal can rotate about the CC bond. The values of ρ_0 and U_0 determined from the second virial coefficient are

$$\rho_0 = 4.2 \text{ A} \qquad U_0/k = 256° \text{ K}$$

The crystal of ethylene belongs to the orthorhombic system which is not far from tetragonal (Fig. 7). If we approximate

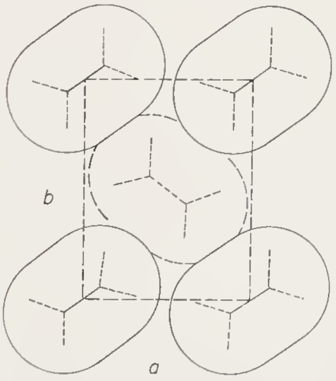

Fig. 7. Body-centered orthorhombic crystal structure of ethylene.

the real lattice by a tetragonal body-centered lattice of the class D_{4h}, the crystal constants are calculated to be

$$\text{cohesive energy} = -3.8 \text{ kcal/mol}$$
$$a = b = 5.8 \text{ A} \qquad c = 4.3 \text{ A}$$

The cohesive energy thus obtained is 16% higher than the observed value. The agreement can be improved by choosing a somewhat larger core (cf. Fig. 5).

VII. MULTIPOLE INTERACTIONS IN CRYSTALS

A. Interaction between Permanent Multipoles

The molecules considered in preceding sections have electric multipoles. These multipoles need not be considered in gaseous states, because their interactions are cancelled when averaged over the isotropic distribution of molecular orientations. The electric multipole interaction, however, plays an important role in the crystalline state. This fact is most clearly understood when the molecules are convex.

Molecules with spherical symmetry crystallize into a close-packed structure. Thus neon, argon, krypton and xenon crystallize into the face-centered cubic lattice of the class O_h. Furthermore, almost spherical molecules such as methane CH_4 and adamantane (sym-tricyclodecane) $(CH_2)_6(CH)_4$ crystallize into the face-centered cubic lattice of the class T_d.

Silicon tetrafluoride, SiF_4, and hexamethylenetetramine, $(CH_2)_6N_4$, are both nearly spherical like methane and adamantane (Fig. 8).

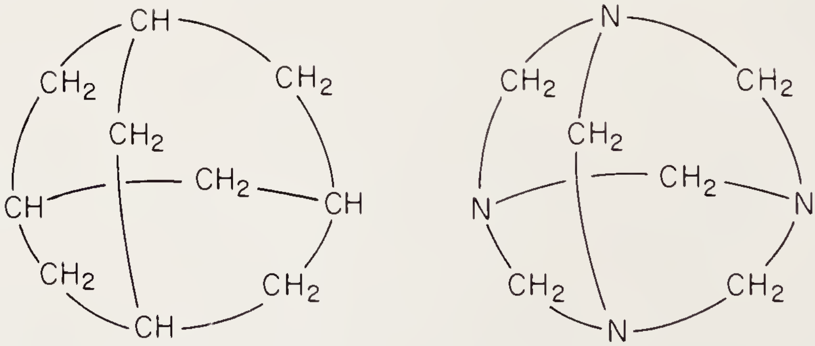

Fig. 8. Two nearly spherical molecules, adamantane and hexamethylenetetramine, for which crystal structures are different.

Their crystal structure, however, is not close-packed; it is the body-centered cubic lattice of the class T_d, in which molecules are in parallel orientations (Fig. 9). These molecules have strong electric octupoles and the octupolar attraction makes the energy of the body-centered lattice lower than the close-packed face-centered lattice.

Crystals of carbon dioxide, CO_2, β-hexachlorocyclohexane, $C_6H_6Cl_6$, and β-hexabromocyclohexane, $C_6H_6Br_6$, have face-centered cubic structure of the class T_h. The molecular axes are distributed equally in four orientations (1,1,1), (1,1,—1), (1,—1,1), and (—1,1,1); the structures are not close packed for these prolate and oblate molecules (Fig. 10). They have strong electric quadrupoles and higher multipoles, and the multipolar interaction lowers the energy of the face-centered lattice. In fact, if carbon dioxide crystallized into a close-packed lattice, keeping the molecular axes parallel, then the quadrupolar interaction, which is repulsive in this case, would reduce its total cohesive energy.

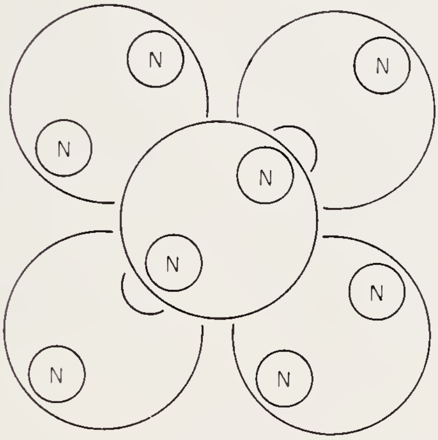

Fig. 9. Molecular orientation in the body-centered cubic crystal of hexamethylenetetramine.

It has been found by the present author that these multipole interactions can be demonstrated by models of molecules with magnetic multipoles. Molecules of carbon dioxide and cyclohexane hexahalides are represented respectively by prolate and oblate "spherocylinders" each composed of two magnetized pieces of barium ferrite as shown in Figs. 11(a) and (b). A cluster of several such quadrupolar models crystallizes into a correct face-centered cubic structure (with a cohesive force greater than the gravity) which is satisfactorily stable against disturbances. These photographs are given in Figs. 12 and 13.

A sphere which is composed of eight pieces of magnet as in Fig. 11(c) represents hexamethylenetetramine. A cluster of several

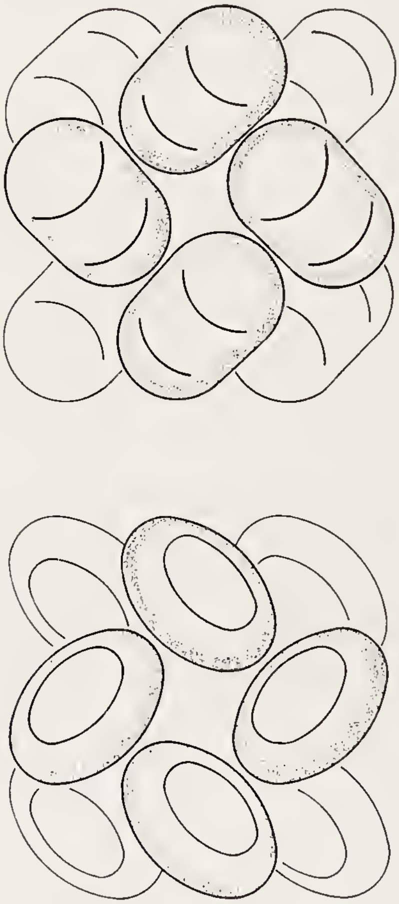

Fig. 10. Molecular orientations in the face-centered cubic crystals of carbon dioxide (top) and cyclohexane hexahalides.

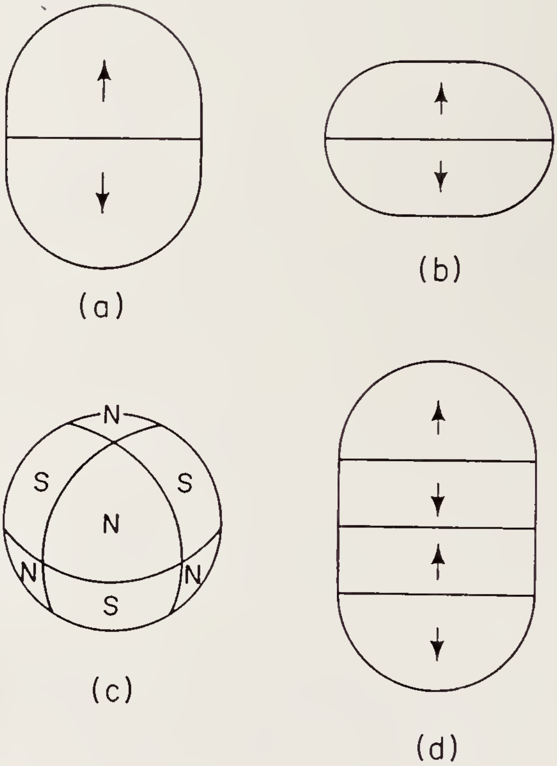

Fig. 11. (a) Prolate quadrupolar molecule which crystallizes into a face-centered cubic structure as shown in Fig. 12. (b) Oblate quadrupolar molecule which crystallizes into a face-centered cubic structure as shown in Fig. 13. (c) Spherical octupolar molecule which crystallizes into a body-centered cubic structure as shown in Fig. 14. (d) Prolate multipolar molecule which crystallizes into orthorhombic and monoclinic structures shown in Fig. 15.

such octupolar spheres crystallizes into a body-centered cubic structure characteristic of hexamethylene tetramine or silicon tetrafluoride, as seen in Fig. 14.

A parallel body of a regular octahedron embracing six pieces of magnet in symmetry represents uranium hexachloride, UCl_6, and

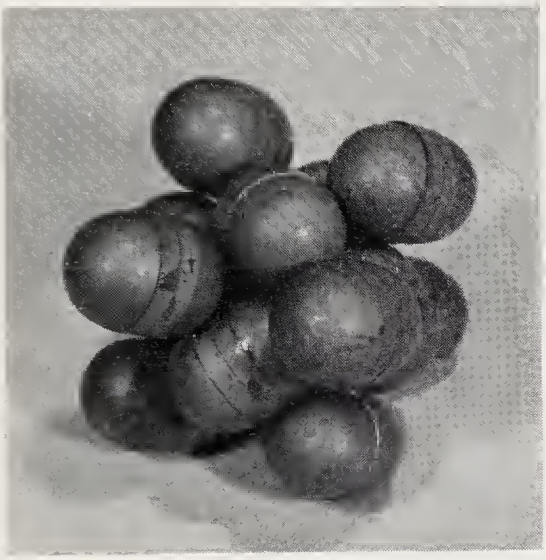

Fig. 12. Face-centered cubic crystal of convex ferrite "molecules" indicating carbon dioxide.

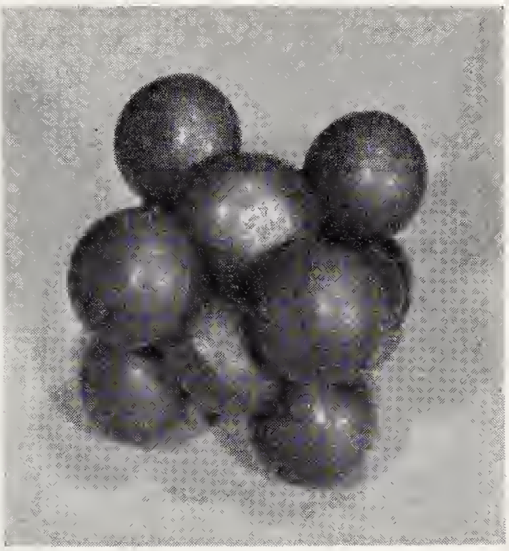

Fig. 13. Face-centered cubic crystal of convex ferrite molecules indicating cyclohexane hexahalides.

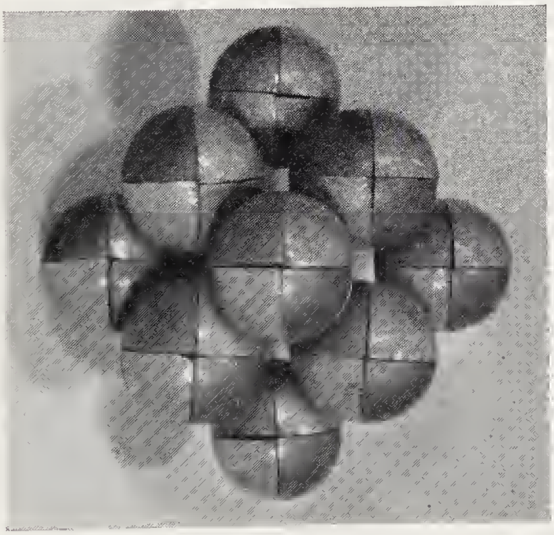

Fig. 14. Body-centered cubic crystal of convex ferrite molecules indicating hexamethylenetetramine.

wolfram hexachloride, WCl_6. A cluster of these models can be arranged into either a hexagonal or a trigonal lattice as shown in Fig. 15. The former arrangement is of the class D_{3d} and represents the crystal structure of UCl_6; the latter is of the class C_{3i} and represents the crystal structure of WCl_6.

A prolate spherocylinder, which is composed of four pieces of magnet as in Fig. 11(d), represents several kinds of linear and nearly linear molecules. A cluster of these models can be arranged into several kinds of crystal structure. One structure, which is shown in Fig. 16(a), is orthorhombic D_{2h}^{18} and corresponds to crystals of chlorine, Cl_2, bromine, Br_2, iodine, I_2, and

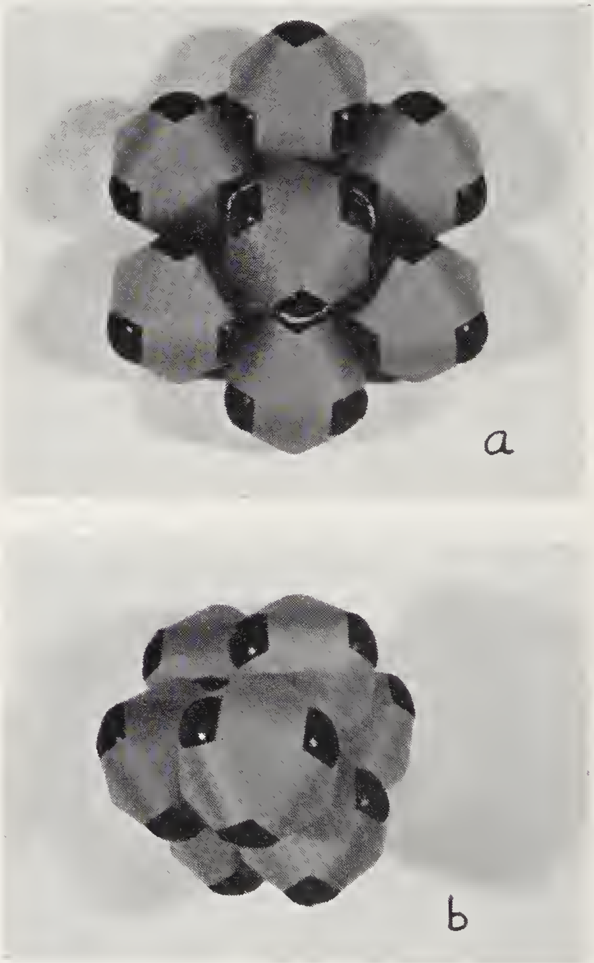

Fig. 15. Hexagonal and trigonal crystals of convex models of molecules, (a) corresponding to uranium hexachloride, (b) to wolfram hexachloride.

hexamethylenediamine, $NH_2(CH_2)_6NH_2$. Another structure is orthorhombic D_{2h}^{15}, shown in Fig. 16(b), to which the crystal of p-diiodobenzene, p-$C_6H_4I_2$, belongs. A third structure is monoclinic C_{2h}^{5}, shown in Fig. 16(c), to which many kinds of molecular crystals belong, e.g., dicyanoacetylene, $C_2(CN)_2$, p-dibromobenzene, p-$C_6H_4Br_2$, p-dichlorobenzene, p-$C_6H_4Cl_2$, p-benzoquinone, p-$C_6H_4O_2$, and p-dinitrobenzene, p-$C_6H_4(NO_2)_2$.

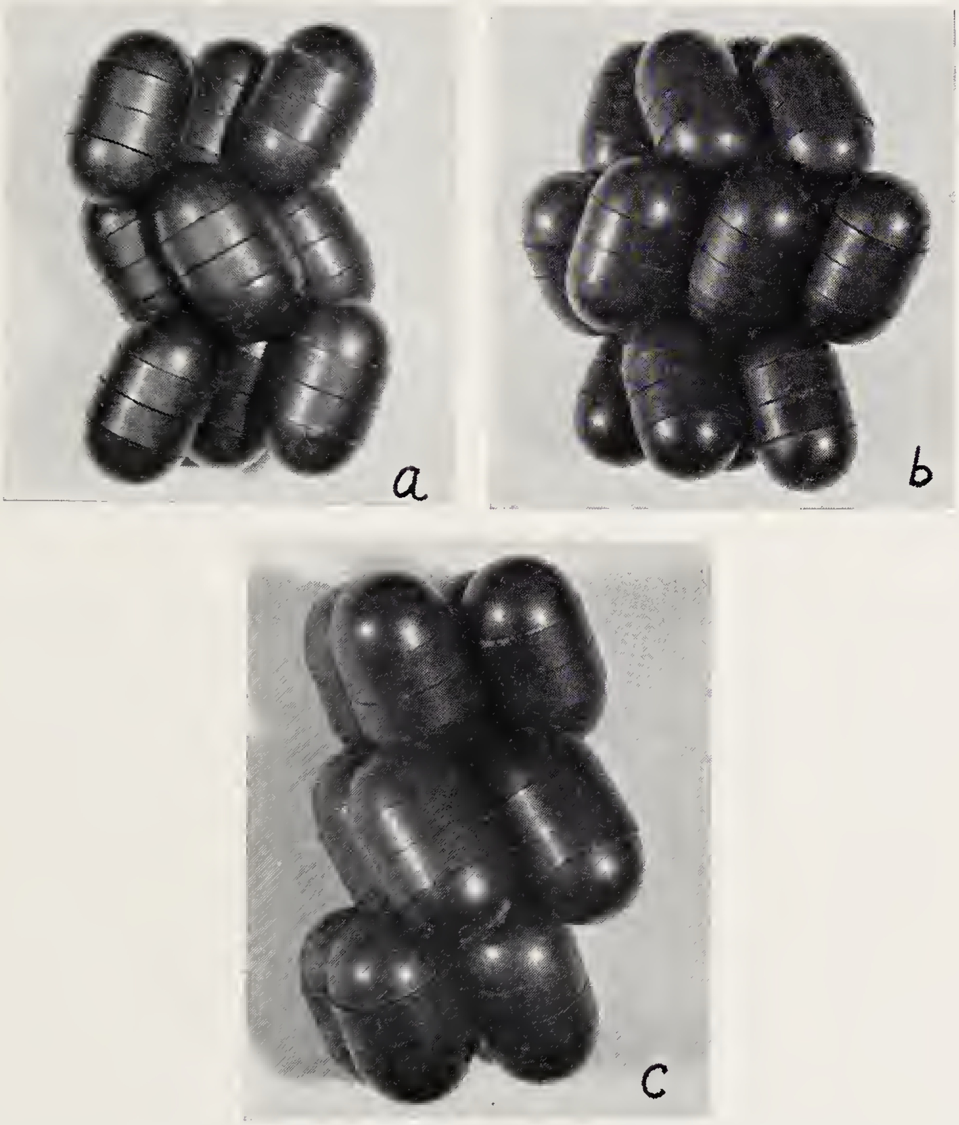

Fig. 16. Orthorhombic and monoclinic crystals of convex ferrite molecules. Space groups are D_{2h}^{18}, D_{2h}^{15}, and C_{2h}^{5} for (a), (b), and (c).

B. Stability of Cubic Close Packing for Heavy Rare-Gas Atoms

There have been several attempts to explain the stability of the cubic close packing for rare-gas atoms over the hexagonal close-packing (excepting helium for which quantum effects are predominant).

If the potential is assumed to be additive and if only the first-neighbor interaction in a crystal is considered, then the cubic and hexagonal close-packed structures have equal cohesive energies, because in both cases an atom has the same number (twelve) of first neighbors.

Interactions between second and farther neighbors were calculated in detail by Kihara and Koba.[17] It was shown, however, that the stability of the cubic close-packed lattice does not follow from the additive potential

$$U(r) = \frac{U_0}{s-6}\left[6\left(\frac{r_0}{r}\right)^s - s\left(\frac{r_0}{r}\right)^6\right] \tag{49}$$

for any value of s greater than 6 nor from the potential

$$U(r) = \frac{U_0}{\sigma-6}\left[6 \exp\frac{\sigma(r_0-r)}{r_0} - \sigma\left(\frac{r_0}{r}\right)^6\right] \tag{50}$$

for $\sigma > 8.675$. For these potentials the hexagonal close-packed lattice is more stable, although it is favored over the cubic by only 0.01% of the cohesive energy. The cubic close-packed lattice becomes more stable than the hexagonal for σ less than 8.675 in Eq. (50). But a potential with $\sigma < 8.675$ has too wide a bowl to be accepted as a very accurate two-body intermolecular potential. This work was supplemented and confirmed by Jansen and Dawson,[18] who took account of the zero-point energy.

Explanation of the stability of the cubic crystals on the basis of a two-body potential function was thus unsuccessful. As a next step three-body interactions were considered by several authors. Axilrod[19] summed the triple-dipole interaction, a non-additive part of the van der Waals attraction, in both the cubic and hexagonal close packings. He concluded: "The difference in the triple-dipole interaction for the cubic and hexagonal close-packed lattices, although favoring the former structure, is less than 0.01% of the cohesive energy and hence cannot account for the structure of these rare-gas solids."

The second and third virial coefficients in the equation of state of rare gases calculated by the use of Eq. (49) with $s = 12$ agree with observed values when the nonadditivity of the intermolecular potential is taken into account.[20] If we assume additivity, on the other hand, then we must use an effective intermolecular potential with a wider bowl in order to explain the temperature dependence of the third virial coefficient.[21] In other words, the influence of nonadditivity of the intermolecular potential can, to some extent, be eliminated by using an effective (additive) intermolecular potential with a wider bowl. An appropriate choice seems to be not far from Eq. (50) with $\sigma = 8.675$, for which the two structures of close packing have exactly equal cohesive energies.

Thus we have seen that no essential difference exists between cubic and hexagonal cohesive energies as long as a central force is assumed between molecules. An alternative approach is therefore needed; noncentral forces must be considered, as was pointed out by Prins *et al.*[22] and Barron and Domb.[23] An explanation by the present author[24] is the following.

A rare-gas atom is spherically symmetric in free space, but not in a crystal because of the compression by surrounding atoms. An atom in a close-packed lattice has twelve nearest neighbors and has six "windows" facing the second neighbors (Fig. 17). At these windows the electron density should be different from other parts, and hence the atom has an electrical multipole. It is easily seen that, in a hexagonal close-packed lattice, this multipole is an octupole and the octupole interaction between first neighbors is repulsive. In a cubic close-packed lattice, on the other hand, an atom has a higher symmetry, the lowest-order nonvanishing

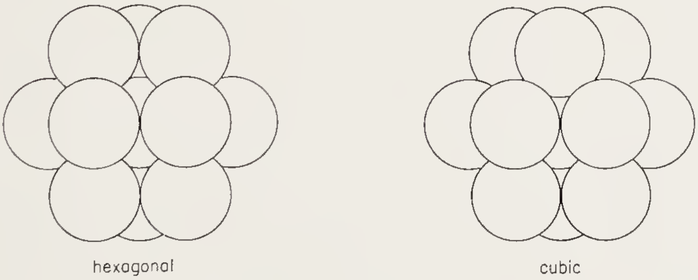

Fig. 17. First neighbor configurations for hexagonal and cubic close packings.

multipole being hexadecapole. Although this hexadecapole interaction is also repulsive, the effect is definitely smaller than the octapole repulsion in the hexagonal case.

Thus we reach the following conclusion: *The stability of the cubic close-packed structure of heavy rare-gas crystals is due to the repulsion between electrical octupoles induced in atoms in the hexagonal case.*

VIII. ACKNOWLEDGMENT

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THEORIES ON THE MAGNETIC PROPERTIES OF COMPOUNDS

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I. INTRODUCTION

Magnetic properties of compounds are of great importance when atoms or ions with permanent magnetic dipole moment are involved, because they reflect the effects of the crystal environments on the atoms or ions. By analyzing its magnetic behavior we can get information about the structure of the substance.

The atomic permanent magnetic dipole arises from a partly-filled inner shell of electrons, which occurs in the elements of the transition groups. Of these the iron group with incomplete $3d$

shell has been most fully investigated. In the present article, therefore, we shall mainly deal with the compounds of 3*d* group metals.

The first half will be devoted to the magnetic behavior of the individual ions. In paramagnetic substances mutual interaction of the magnetic ions plays a subordinate role, and the system can be treated as an assembly of almost independent tiny magnets. The magnetic behavior of the individual ions is manifested directly in the macroscopic magnetic properties of such crystals. One can, therefore, elucidate the microscopic natures of such ions by analyzing the experimental data on the paramagnetic (i.e., magnetically dilute) compounds. In this sense, it would be of fundamental importance to investigate the magnetic properties of the individual ions in paramagnetic substances.

The paramagnetic ions in crystals are investigated extensively in two ways: through study of optical spectra and of magnetic properties including paramagnetic resonance phenomena. The former is concerned mainly with higher excited states of the ions and the recent advances have been admirably covered in a review article by McClure[51] (see also ref. 52). For the latter, which is mainly concerned with the lowest-lying states, there are also many review articles.[43,69] One of the purposes of the present article lies in reviewing these two fields from a more unified point of view. Consequently, detailed analyses of the individual substances are not intended in the following. Instead, emphasis is laid on the various kinds of interactions responsible for yielding important information about the structure of the substances.

The rest of the article will be devoted to discussion of the various possible mechanisms for the interionic interaction, especially those in the antiferromagnetic substances. The theories in this area are less quantitative than those on the paramagnetic substances because of the mathematical difficulties involved in the calculations. This situation makes the aspect of the theories on the interionic interactions quite different from that of the theories on the paramagnetic substances, i.e., on the intra-ionic interactions. The gap between these two fields should be filled in order to reinforce one by the other. One of the aims of the present work is to connect the theories in both fields as smoothly as possible.

II. PARAMAGNETIC SUSCEPTIBILITIES

Letting the magnetic moment of an ion be denoted by $\boldsymbol{\mu}$ and disregarding the interionic interactions, we obtain the molar magnetic susceptibility of the compound by the well-known Langevin formula or Curie's law

$$\chi_{\text{mol}} = N\boldsymbol{\mu}^2/3kT \tag{1}$$

where N denotes Avogadro's number.

The moment $\boldsymbol{\mu}$ arises from the incomplete shell of the magnetic ion and its value in crystal is generally different from that of the free ion. The difference has been of great significance in clarifying the electronic structure of the ions in crystals. In the case of a free ion, the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is a constant of motion, and the values of $\mathbf{L}$ and $\mathbf{S}$ for the ground state are determined by Hund's rule.* Its magnetic moment $\boldsymbol{\mu} = -\beta(\mathbf{L} + 2\mathbf{S})$ is generally not parallel to $\mathbf{J}$, and the parallel component μ_J is given by

$$\mu_J = -g_J\beta J \tag{2}$$

where

$$g_J = 3/2 + [S(S + 1) - L(L + 1)]/2J(J + 1) \tag{3}$$

is the so-called Landé g factor and β is the Bohr magneton. If we neglect the effects of the perpendicular component of μ, which yields a small temperature-independent part of the susceptibility,[43,93] Langevin's formula is expressed as

$$\chi_{\text{mol}} = Ng_J^2\beta^2J(J + 1)/3kT \tag{4}$$

The susceptibilities of the rare-earth compounds conform approximately to the above formula,[74,93] and the deviation from it can be ascribed to the influence of the surroundings to the motion of **J**, which can be treated by the usual perturbation method.[19,65,94]

---

* Of the possible terms allowed by the Pauli principle, that with the maximum multiplicity lies lowest and its multiplicity is $2S + 1$.

If there are several possible ways in which $\mathbf{L}$ and $\mathbf{S}$ be coupled so as to maintain the maximum multiplicity, then the lowest-lying term is that with the maximum value of L.

If the incomplete shell is less than half full, the multiplets are normal, i.e., the smallest J has lowest energy hence $J = L - S$. For shells more than half full the largest J lies lowest and $J = L + S$.

The situation is quite different for the ions with incomplete *d* shells. In most of these cases the susceptibility data approximately fit the formula for the vanishing **L**, i.e.,

$$\chi_{\text{mol}} = 4N\beta^2 S(S + 1)/3kT \tag{5}$$

This "quenching of the orbital angular momentum" is one of the most remarkable features of the magnetic ions in crystals.

In some compounds (cyanides of the iron group elements are the typical examples), magnetic susceptibilities are much smaller than those expected from the formula (5). To get good agreement with the experiment one has to insert an S value smaller than the one determined by Hund's rule for the free ion. Such compounds are sometimes called low-spin compounds.

Most of these features are well accounted for by assuming an electrostatic field with proper symmetry acting on the electrons in the *d* shell.[72,94] This field is called crystalline field (or crystal field, sometimes ligand field) and expresses the influence of the environment as an electrostatic field. The splitting of the energy levels in the crystalline field was discussed by Bethe[6] in great detail. The orbital degeneracy of the term ^{2S+1}L will be completely removed by the field with sufficiently low symmetry and the ground level becomes an orbital singlet. Thus only the $(2S + 1)$-fold spin degeneracy will remain in the ground level, and the magnetic behaviors of such an ion will be like those of the $L = 0$ state.

Though (5) is convenient for seeing the general aspect of the magnetic susceptibility, it is not precise from a quantitative point of view. In order to calculate the susceptibility in more detail, one has to calculate the magnetization according to the usual averaging procedure of quantum statistical mechanics as follows:

$$\bar{M} = N \frac{\operatorname{Tr} \mu_z \exp\left[-(H_0 - \mu_z \mathscr{H}_z)/kT\right]}{\operatorname{Tr} \exp\left[-(H_0 - \mu_z \mathscr{H}_z)/kT\right]} \tag{6}$$

where H_0 is the unperturbed Hamiltonian and $-\mu_z \mathscr{H}_z$ is the Zeeman energy due to the external magnetic field along the z axis. Consider a representation in which H_0 is diagonal. Let the eigenvalues of H_0 be $E_0 = 0, E_1, E_2, \ldots, E_n, \ldots$. Then the susceptibility is

$$\chi_{\mathrm{mol}} = \frac{\overline{M}}{\mathscr{H}_z} = \frac{N \sum\limits_{n,n'} |(\mu_z)_{n,n'}|^2 [\exp(-E_{n'}/kT) - \exp(-E_n/kT)]/(E_n - E_{n'})}{\sum\limits_n \exp(-E_n/kT)} \tag{7}$$

Thus the susceptibility data give the indirect information about the low-lying energy levels of the paramagnetic ions in crystals.

Equation (7) is the formula which must be used in the most general case. However, we can simplify it by assuming that the states are divided into two groups.[93] The states in the first group are those whose Boltzmann factor $\exp(-E_n/kT)$ is appreciably different from zero, i.e., its excess of energy over the lowest state is either smaller than or comparable with kT. We indicate the states in the first group by the subscript l. The states in the second group are those whose energies exceed the energies of the states in the first group by an amount large compared to kT. We indicate them by the subscript h. Then (7) can be reduced to

$$\chi_{\mathrm{mol}} = \frac{N \sum\limits_{l,l'} |(\mu_z)_{l,l'}|^2 \exp(-E_l/kT)}{kT \sum\limits_{l} \exp(-E_l/kT)} + \frac{2N \sum\limits_{l,h} |(\mu_z)_{l,h}|^2 \exp(-E_l/kT)(E_h - E_l)}{\sum\limits_{l} \exp(-E_l/kT)}$$
$$\equiv N\overline{\mu_z^2}/kT + \chi_0 \tag{8}$$

where χ_0 represents the temperature-independent susceptibility first derived by Van Vleck.[93] When all states in the ground term (the values of L and S are given according to Hund's rule) are included in the first group, we obtain

$$\overline{\mu_z^2} = \beta^2\overline{(L_z + 2S_z)^2} = \beta^2[L(L+1) + 4S(S+1)]/3 \tag{9}$$

and

$$\chi_{\mathrm{mol}} = \{N\beta^2[L(L+1) + 4S(S+1)]/3kT\} + \chi_0 \tag{10}$$

On the other hand, when only the ground states (the values of optimum J is given) are included in the first group, we obtain

$$\overline{\mu_z^2} = \beta^2\overline{(L_z + 2S_z)^2} = \beta^2 g^2 J(J + 1)/3 \tag{11}$$

and

$$\chi_{\text{mol}} = [N\beta^2 J(J + 1)/3kT] + \chi_0 \tag{12}$$

which is the same as (4) except the last term.

More direct information can be obtained by the electron-spin resonance (paramagnetic resonance) method, in which the magnetic dipole transitions between the levels arising from the lowest states by the Zeeman splitting are observed as the resonance absorptions. This powerful method has been extensively applied to various paramagnetic salts, and the results are summarized in excellent review articles by the Oxford group.[8,9,62] The reader is also referred to the recent interesting book by Low.[50]

III. ENERGY LEVELS IN CRYSTAL FIELD (I)

In the case of rare-earth ions, the incomplete $4f$ shells are embedded in the $5s$ and $5p$ shells so that the crystalline field effect is much weaker than the spin-orbit interaction of the f electrons which couples **L** and **S** into **J**. This may therefore be classified

TABLE I. Resolution of the $(2L + 1)$-Dimensional Representation

D^L	S	P			D					F			
	A_1	T_1			E		T_2			A_2	T_1		
		x	y	z	u	v	ξ	η	ζ		x	y	z
$M_L = 4$													
3											$-\sqrt{5/4}$	$-i\sqrt{5/4}$	
2						$1/\sqrt{2}$			$-i/\sqrt{2}$	$1/\sqrt{2}$			
1		$-1/\sqrt{2}$	$i/\sqrt{2}$				$i/\sqrt{2}$	$-1/\sqrt{2}$			$\sqrt{3/4}$	$-i\sqrt{3/4}$	
0	1			1	1								1
-1		$1/\sqrt{2}$	$i/\sqrt{2}$				$i/\sqrt{2}$	$1/\sqrt{2}$			$-\sqrt{3/4}$	$-i\sqrt{3/4}$	
-2						$1/\sqrt{2}$			$i/\sqrt{2}$	$-1/\sqrt{2}$			
-3											$\sqrt{5/4}$	$-i\sqrt{5/4}$	
-4													

Phases of the (LM_L) functions are taken to agree as the weak-field case. In the following we shall restrict our attention to d electrons.

We shall start with the so-called intermediate-field case. In many of the ionic complexes of the $3d$-group elements, while the free ion energies due to the Coulomb repulsion between electrons have the order of magnitude of 10^4 to 10^5 cm^{-1}, energies of the cubic crystal field are of the order of 10^4 cm^{-1}. So we can treat the effect of the latter as the perturbation acting on the multiplet terms characterized by definite values of L and S.

When the free ion is subjected to the cubic field, each level specified by L value will be split into sublevels. The states which arise from an atomic state characterized by L can be determined group-theoretically by making use of the character tables of the point groups. These are given in Table I. For practical purposes, however, it is often necessary to know the transformation coefficients between the $|SLM_LM_S)$ and $|S\Gamma M_S\gamma)$ schemes, where Γ is the symbol for the irreducible representation of the octahedral group and γ specifies the bases of the representation Γ. These are also given in Table I. The phases of the (LM_L) functions, which can be regarded as the bases of the $(2L + 1)$-dimensional representation of the rotation group and are isomorphic to the spherical harmonics Y_{LM_L}, are taken to agree with those given by Condon and Shortley.[12]

of the Rotational Group into Irreducible Representation of O_h Group

			G								
T_2			A_1	E		T_1			T_2		
ξ	η	ζ		u	v	x	y	z	ξ	η	ζ
			$\sqrt{(5/24)}$	$\sqrt{(7/24)}$				$-i/\sqrt{2}$			
$\sqrt{3}/4$	$-i\sqrt{3}/4$					$-i/4$	$1/4$		$-i\sqrt{7}/4$	$-\sqrt{7}/4$	
		$1/\sqrt{2}$			$1/\sqrt{2}$						$i/\sqrt{2}$
$\sqrt{5}/4$	$i\sqrt{5}/4$					$-i\sqrt{7}/4$	$-\sqrt{7}/4$		$i/4$	$-1/4$	
			$\sqrt{(7/12)}$	$-\sqrt{(5/12)}$							
$-\sqrt{5}/4$	$i\sqrt{5}/4$					$-i\sqrt{7}/4$	$\sqrt{7}/4$		$i/4$	$1/4$	
		$1/\sqrt{2}$			$1/\sqrt{2}$						$-i/\sqrt{2}$
$-\sqrt{3}/4$	$-i\sqrt{3}/4$					$-i/4$	$-1/4$		$-i\sqrt{7}/4$	$\sqrt{7}/4$	
			$\sqrt{(5/24)}$	$\sqrt{(7/24)}$				$i/\sqrt{2}$			

with those given in Condon–Shortley's book.[12]

There can also be nonvanishing matrix elements of the crystal field potential between the states arising from the different multiplets if they belong to the same representation of the octahedral group.* These are given by Finkelstein and Van Vleck[18] for d^3 and d^7 and by Orgel[60] for the rest configurations. By diagonalizing the matrix of the free ion energy, which is diagonal in $|SLM_SM_L)$ scheme, and adding the cubic field potential, we can obtain the energy levels and the eigenfunctions of the ion in the cubic field.

In general the crystalline field is not of perfectly cubic symmetry. Under the action of lower-symmetry field and the spin-orbit coupling between d electrons, each ground level listed in Table I is split into several levels, although at least twofold degeneracy remains if the number of electrons is odd (Kramers' theorem).[44]

TABLE II. The Lowest States of the Iron Group Ions in a Cubic Crystalline Field

Free ion ground state		Intermediate field[a]	Strong field[a]	Ions (ζ, cm^{-1})		λ for free ion, cm^{-1}
$3d^1$	^2D	$^2T_{2g}$ $(d\varepsilon)$		Ti^{3+} (154)		154
$3d^2$	^3F	$^3T_{1g}$ $(d\varepsilon^2)$		V^{3+} (209)		104
$3d^3$	^4F	$^4A_{2g}$ $(d\varepsilon^3)$		Cr^{3+} (276)	V^{2+} (168)	91, 56
$3d^4$	^5D	^5E_g $(d\varepsilon^3 d\gamma)$	$^3T_{1g}$ $(d\varepsilon^4)$	Mn^{3+} (360)	Cr^{2+} (236)	88, 57
$3d^5$	^6S	$^6A_{1g}$ $(d\varepsilon^3 d\gamma^2)$	$^2T_{2g}$ $(d\varepsilon^5)$	Fe^{3+} (?)	Mn^{2+} (335)	—
$3d^6$	^5D	$^5T_{2g}$ $(d\varepsilon^4 d\gamma^2)$	$^1A_{1g}$ $(d\varepsilon^6)$		Fe^{2+} (404)	−103
$3d^7$	^4F	$^4T_{1g}$ $(d\varepsilon^5 d\gamma^2)$	^2E_g $(d\varepsilon^6 d\gamma)$		Co^{2+} (528)	−178
$3d^8$	^3F	$^3A_{2g}$ $(d\varepsilon^6 d\gamma^2)$			Ni^{2+} (644)	−324
$3d^9$	^2D	$^2T_{2g}$ $(d\varepsilon^6 d\gamma^3)$			Cu^{2+} (829)	−829

[a] The configurations given in the parentheses are the main components of the respective states.

These splittings are usually of the order of a few hundred to 1000 cm^{-1} when there is orbital and spin degeneracy, but $\sim$1 cm^{-1} if there is only spin degeneracy (e.g., Mn^{2+}). General treatment of these splittings is rather tedious. However, a great deal of labor can be saved in the calculation of the matrix elements if we use the "operator equivalents" of these. As is well known,[12] the spin-orbit interaction energy $\sum_i \zeta \mathbf{l}_i \cdot \mathbf{s}_i$ can be replaced by the operator $\lambda \mathbf{L} \cdot \mathbf{S}$ in the calculation of the matrix elements between the states arising from the same (L, S) term. Similarly, it is shown by Stevens *et al.*[15,27,84] that the crystal field potential functions can also be replaced by equivalent operators expressed in terms of L_x, L_y, and L_z $(= M_L)$. The explicit forms of the operators are listed in the review articles.[8,50]

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* The effects of the admixed higher terms are usually neglected in analyzing the ESR spectra of high spin compounds.

IV. ENERGY LEVELS IN CRYSTAL FIELD (II)

There is another approach to the problem of magnetic ions in crystals.[88–90] This method is more appropriate for handling the case of strong crystalline field and can be extended to include the covalency between the magnetic ion and its surroundings.[95] In this treatment the effect of the crystalline field is taken into account in advance of the Coulomb repulsion between electrons. If a d electron is considered as moving in an electrostatic field with nonspherical symmetry, the fivefold degeneracy of the single electron d orbitals is removed. In the case of the cubic field, the d orbitals are split into a doublet denoted by $d\gamma$ and a triplet denoted by $d\varepsilon$. The two $d\gamma$ orbitals have the angular dependence proportional to $(3z^2 - r^2)/r^2$ and $(x^2 - y^2)/r^2$, and have their lobes of electron density concentrated along the z axis and x and y axes, respectively, where these coordinate axes are taken to direct towards the surrounding anions or atoms. Angular dependences of the three $d\varepsilon$ orbitals are yz/r^2, zx/r^2, and xy/r^2, and these have lobes of electron cloud pointing in between the coordinate axes. In the simple ionic model for the octahedrally surrounded ion, the $d\gamma$ orbitals are higher than the $d\varepsilon$ (vice versa in the tetrahedral case) and the energy difference is expressed by Δ or $10Dq$. The $d\gamma$ and $d\varepsilon$ orbitals belong to the representations E_g and T_{2g} of the octahedral group respectively.

By accommodating the d electrons in these orbitals, one can set up various wave functions of the total system. Taking account of the mutual repulsion between electrons, the functions with the same symmetry (belonging to the same representation) combine with each other. The secular matrices of this eigenvalue problem are extensively calculated by Tanabe and Sugano[89] (see also ref. 51).

While the spins of the electrons tend to be parallel to each other due to the intra-ionic Coulomb (exchange) interaction (Hund's rule), the electrons are disposed to lie in the lower $d\varepsilon$ orbitals as the result of the splitting by the crystalline field. The character of the ground state of the ion will thus be determined by the counterbalance of these two effects. If the splitting Δ is large enough, all the electrons will occupy the lower $d\varepsilon$ subshell provided the number of electrons is less than six. In this case (strong-field case), the resultant S value of the ion will be smaller than that given by Hund's rule for the free ion (low-spin compounds).

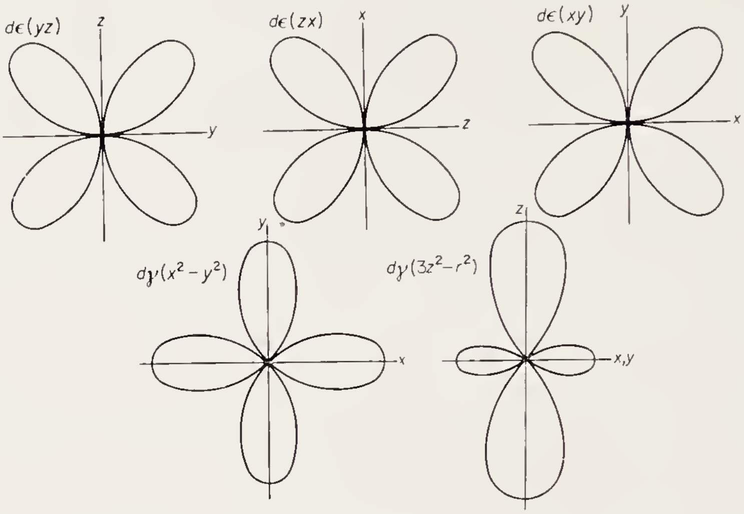

Fig. 1. Diagrams of the charge clouds associated with orbitals of a d electron on a paramagnetic ion.

The above method of approach was first proposed by Van Vleck concerning the susceptibility of ferricyanides,[95] and detailed treatments have been given by Howard[24] and by Kamimura[28] for the complexes. This procedure has been developed by Kotani to account for the temperature dependence of the susceptibilities of various low-spin compounds.[42] Griffith recently extended Kotani's calculation to the high-spin compounds.[21] For $4d$ and $5d$ metal ions, the spin–orbit interaction is much stronger than the $3d$ electrons and has the comparable order of magnitude with the Coulomb repulsion.[17] Susceptibility calculation for these group

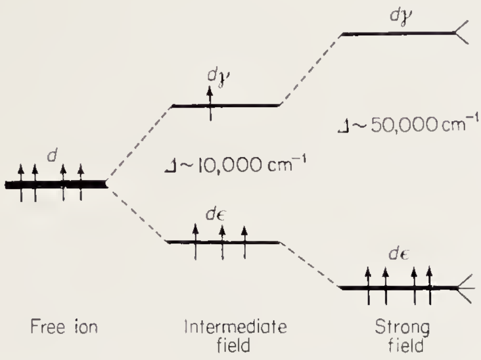
dγ
dγ
Δ ~ 50,000 cm⁻¹
d
Δ ~ 10,000 cm⁻¹
dε
dε
Free ion
Intermediate field
Strong field

Fig. 2. The energy levels of a single *d* electron on a free ion shown on the left split into two sublevels if the ion is placed in a cubic crystalline field. Distribution of the electrons in these levels is illustrated by arrows for the d^4 configuration.

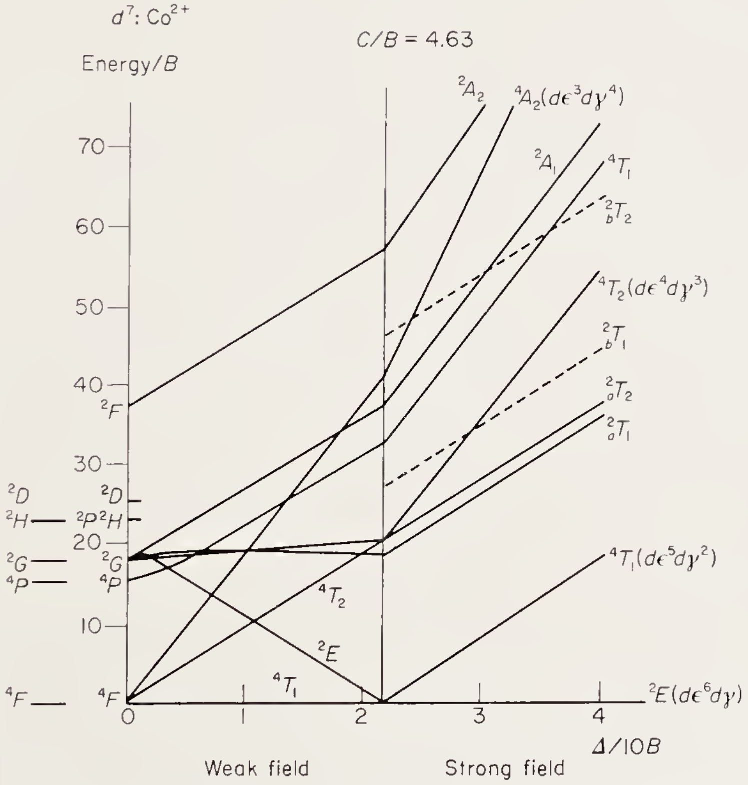

Fig. 3. Energy levels for d^7 (Co^{2+}) in a cubic field.

ions has also been carried out quite recently for the cubic field case.[29] It should be noted here that, as far as the effect of the $d\gamma$ orbitals is neglected, the orbital angular momentum of the $d\varepsilon$ electrons can be treated quite analogously to that of the p electrons except that a $d\varepsilon$ electron behaves as a p electron with positive charge.[43]

The calculation of the matrix elements of the lower symmetry fields and of the spin–orbit interaction is not so easy. The general procedure is given by Tanabe and Kamimura and the tables for this purpose are also given in their papers.[87,88]

Group-theoretical consideration shows that, to the first order, only the multiplets ${}^{2S+1}T_1$ and ${}^{2S+1}T_2$ with $S \geqslant \frac{1}{2}$ are split by the spin–orbit interaction. Corresponding to the effective spin–orbit coupling Hamiltonian $\lambda \mathbf{L} \cdot \mathbf{S}$ in the weak-field scheme

TABLE III. Spin–Orbit Interaction Parameters in the Strong Field Scheme[87]

n	Configuration	${}^{2S+1}\Gamma$	λ/ζ
1	$d\varepsilon$	${}^2T_2$	1
2	$d\varepsilon^2$	${}^3T_1$	$-\frac{1}{2}$
	$d\varepsilon d\gamma$	${}^3T_1$	$\frac{1}{4}$
	$d\varepsilon d\gamma$	${}^3T_2$	$-\frac{1}{4}$
3	$d\varepsilon^2({}^3T_1)d\gamma$	${}^4T_1$	$\frac{1}{6}$
	$d\varepsilon^2({}^3T_1)d\gamma$	${}^4T_2$	$-\frac{1}{6}$
	$d\varepsilon d\gamma^2({}^3A_2)$	${}^4T_1$	$-\frac{1}{3}$
4	$d\varepsilon^2({}^3T_1)d\gamma^2({}^3A_2)$	${}^5T_2$	$\frac{1}{4}$
5	$d\varepsilon^4({}^3T_1)d\gamma$	${}^4T_1$	$-\frac{1}{6}$
	$d\varepsilon^4({}^3T_1)d\gamma$	${}^4T_2$	$\frac{1}{6}$
	$d\varepsilon^4({}^3T_1)d\gamma$	${}^2T_1$	$-\frac{1}{6}$
	$d\varepsilon^4({}^3T_1)d\gamma$	${}^2T_2$	$\frac{1}{6}$
6	$d\varepsilon^4({}^3T_1)d\gamma^2({}^3A_2)$	${}^5T_2$	$-\frac{1}{4}$
	$d\varepsilon^5 d\gamma$	${}^3T_1$	$-\frac{1}{4}$
	$d\varepsilon^5 d\gamma$	${}^3T_2$	$\frac{1}{4}$
7	$d\varepsilon^5 d\gamma^2({}^3A_2)$	${}^4T_1$	$\frac{1}{3}$
	$d\varepsilon^4({}^3T_1)d\gamma^3$	${}^4T_1$	$-\frac{1}{6}$
	$d\varepsilon^4({}^3T_1)d\gamma^3$	${}^4T_2$	$\frac{1}{6}$
8	$d\varepsilon^5 d\gamma^3$	${}^3T_1$	$-\frac{1}{4}$
	$d\varepsilon^5 d\gamma^3$	${}^3T_2$	$\frac{1}{4}$
	$d\varepsilon^4({}^3T_1)d\gamma^4$	${}^3T_1$	$\frac{1}{2}$
9	$d\varepsilon^5 d\gamma^4$	${}^2T_2$	-1

discussed in Section III, Tanabe introduced the following effective Hamiltonian:[87]

$$H_{\mathrm{so}} = \lambda \mathbf{T} \cdot \mathbf{S}$$

where **T** is a tensor operator with T_{1g} symmetry. It is shown that the above-mentioned correspondence between $d\varepsilon(yz,zx,xy)$ and $p(p_x, p_y, p_z)$ orbital functions holds more generally between the multiplets ${}^{2S+1}T_{1,2}$ and ${}^{2S+1}P$. Thus the spin–orbit interaction $\lambda\mathbf{T} \cdot \mathbf{S}$ splits the multiplet ${}^{2S+1}T_1$ (or ${}^{2S+1}T_2$) in just the same way as $\lambda\mathbf{L} \cdot \mathbf{S}$ (or $-\lambda\mathbf{L} \cdot \mathbf{S}$) does with the atomic multiplet ${}^{2S+1}P$. Therefore, it can be seen that these multiplets are split at most into three sublevels by the first-order spin–orbit interaction. The remaining degeneracy is lifted only by the action of the lower symmetry field or the higher order effect of the spin–orbit interaction or the combined action of both. The coefficient λ is related to the parameter of the original expression $\sum_i \zeta \mathbf{l}_i \cdot \mathbf{s}_i$ as shown in Table III.

V. INTRA-ATOMIC INTERACTIONS

In the last two sections we have reviewed the two ways of approach which ultimately give the same results. The interactions considered are (*1*) the Coulomb repulsion between electrons, (*2*) interaction of the magnetic electrons with the environments, and (*3*) the spin–orbit coupling of the magnetic electrons. The first is responsible for the multiplet splittings of the free ion states and has the order of magnitude of 10^4 to 10^5 cm^{-1}. In the case of d electrons, matrix elements of this part of Hamiltonian are expressed in terms of Racah's parameters B and C which are connected with the Slater integrals by the following definitions.[80,89]

$$B = F_2 - 5F_4 \qquad \text{and} \qquad C = 35F_4 \tag{13}$$

The values of these parameters can be determined empirically by analyzing the free ion spectra.

In the simple crystalline field theory, the influence of the environments is represented by the crystalline electric field, which is dominantly cubic in many cases. If we disregard the lower symmetry parts, the effect of the cubic field is expressed by the parameter Δ or $10Dq$. Several attempts at the nonempirical calculation of the parameter were not very successful because of the many difficulties involved in this kind of calculation.[36,91] In the present stage, therefore, we have to be satisfied with the empirical determination of the values by comparing the calculated eigenvalues with experiments.

In the case of divalent ions, good agreement with experiments can be obtained by adjusting the value of Δ.[90] For the trivalent ions, however, one has to use smaller values of B and C than those obtained for the relevant free ions in order to get good fit with experiments.[90] This reduction, as well as the similar one of the spin–orbit coupling parameter λ, can be ascribed to the covalency effect to be discussed in Section VII.

Now, let us proceed to the smaller terms of the Hamiltonian. The theories for these small interactions have been developed in great detail in connection with the analyses of the electron spin resonance spectra.[8,50]

Pryce considered the spin–spin interaction of the following form.[68]

$$V_{\mathrm{ss}} = 4\beta^2 \sum_{j,k} [(\mathbf{s}_j \cdot \mathbf{s}_k)/r_{jk}^3 - 3(\mathbf{r}_{jk} \cdot \mathbf{s}_j)(\mathbf{r}_{jk} \cdot \mathbf{s}_k)/r_{jk}^5] \tag{14}$$

Within a manifold of the definite (L, S) term, this can be reduced to the form[8]

$$-\rho[(\mathbf{L} \cdot \mathbf{S})^2 + \tfrac{1}{2}(\mathbf{L} \cdot \mathbf{S}) - \tfrac{1}{3}L(L+1)S(S+1)] \tag{15}$$

where ρ is the proportionality constant and has the magnitude of order 1 cm^{-1}.

Now let us consider the interaction of electrons with nuclear spin. First we shall consider the dipolar interaction between electron spin and the nuclear magnetic moment:

$$V_{\mathrm{sN}} = \sum 2\gamma\beta\beta_{\mathrm{N}}[-(\mathbf{s}_j \cdot \mathbf{I})/r_j^3 + 3(\mathbf{s}_j \cdot \mathbf{r}_j)(\mathbf{r}_j \cdot \mathbf{I})/r_j^5] \tag{16}$$

where β_{N} and γ refer to the nuclear magneton and nuclear gyromagnetic ratio, respectively.

Since each term of this expression involves the coordinates and spin of one electron only, the first order expectation value of the V_{sN} can be expressed as the sum of the contribution from each electron. As the contribution of an s electron is anomalous, we shall treat it separately. Let the orbital function of the s electron be denoted by ψ_s, then the first-order expectation value of the interaction between the s electron and the nucleus is given by

$$\varepsilon_s = 2\gamma\beta\beta_{\mathrm{N}} \int \psi_s^2(r)[-(\mathbf{s}\cdot\mathbf{I})/r^3 + 3(\mathbf{s}\cdot\mathbf{r})(\mathbf{r}\cdot\mathbf{I})/r^5]dxdydz \tag{17}$$

Using the method of integration by parts, we can rewrite the term involving s_x in the following manner,

$$\begin{aligned}
&2\gamma\beta\beta_{\mathrm{N}} s_x \int \psi_s^2 \left\{ \frac{\partial}{\partial y} \frac{yI_x - xI_y}{r^3} - \frac{\partial}{\partial z} \frac{xI_z - zI_x}{r^3} \right\} dxdydz \\
&= 2\gamma\beta\beta_{\mathrm{N}} s_x \int \left\{ -\frac{yI_x - xI_y}{r^3} \frac{\partial\psi_s^2}{\partial y} + \frac{xI_z - zI_x}{r^3} \frac{\partial\psi_s^2}{\partial z} \right\} dxdydz \\
&= 2\gamma\beta\beta_{\mathrm{N}} s_x \int \left\{ -\frac{y}{r} \frac{yI_x - xI_y}{r^3} + \frac{z}{r} \frac{xI_z - zI_x}{r^3} \right\} \frac{d\psi_s^2}{dr}\, dxdydz \\
&= -2\gamma\beta\beta_{\mathrm{N}} s_x I_x \int \frac{y^2 + z^2}{r^4} \frac{d\psi_s^2}{dr}\, dxdydz \\
&= -2\gamma\beta\beta_{\mathrm{N}} s_x I_x \frac{2}{3} \int \frac{1}{r^2} \frac{d\psi_s^2}{dr}\, d\mathbf{r} \\
&= 2\gamma\beta\beta_{\mathrm{N}} s_x I_x (8\pi/3) \psi_s^2(0)
\end{aligned} \tag{18}$$

Then

$$\varepsilon_s = (8\pi/3) 2\gamma\beta\beta_{\mathrm{N}} \psi_s^2(0) (\mathbf{s}\cdot\mathbf{I}) \tag{19}$$

This is the well-known Fermi interaction of an s electron with a nuclear spin. Since only the s functions have nonvanishing values at the origin, this anomalous contact interaction is often written in the form

$$V_{\mathrm{Fermi}} = (8\pi/3) 2\gamma\beta\beta_{\mathrm{N}} \delta(\mathbf{r}_j)(\mathbf{s}_j\cdot\mathbf{I}) \tag{20}$$

Similar treatment is not valid for other types of orbitals. Hence the original form (16) has to be used in general.*

Next we shall consider the interaction between nuclear spin and the orbital magnetic moment of electrons. Let the position and the velocity of an electron be **r** and **v**. Then, according to Biot–Savart's law, the magnetic field at the origin created by the electron is

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* The Fermi interaction term is invoked by Abragam and Pryce[1] to account for the anomalous hyperfine structures found in the paramagnetic resonance spectra of the V^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, etc. These authors considered a small amount of admixed configuration $3d^{n-1}4s$ to the usual $3d^n$ in order to explain the hyperfine structure in $Mn^{2+}(^6S)$ salts.

$$\vec{\mathscr{H}}_{\hat{e}} = -(e/cr^3)[\mathbf{r} \times \mathbf{v}] = -(e/mcr^3)[\mathbf{r} \times \mathbf{p}] = -(e/mcr^3)\mathbf{l} \quad (21)$$

The magnetic energy of the nuclear magnetic moment **I** placed in this field is given by

$$-\gamma\beta_{\mathrm{N}}(\mathbf{I} \cdot \vec{\mathscr{H}}\hat{e}) = 2\gamma\beta\beta_{\mathrm{N}}(1/r^3)(\mathbf{l} \cdot \mathbf{I}) \quad (22)$$

Summing up (16), (20), and (22), we obtain the Hamiltonian of the interaction between electrons and the nuclear magnetic moment as

$$V_{\mathrm{N}} = 2\gamma\beta\beta_{\mathrm{N}}\{\sum_j[(\mathbf{l}_j - \mathbf{s}_j) \cdot \mathbf{I}/r_j^3 + 3(\mathbf{r}_j \cdot \mathbf{s}_j)(\mathbf{r}_j \cdot \mathbf{I})/r_j^5] + \sum_k(8\pi/3)\delta(\mathbf{r}_k)(\mathbf{s}_k \cdot \mathbf{I})\} \quad (23)$$

where the sum over j should be taken for the electrons other than s electrons and the sum over k for the s electrons. Equivalent effective Hamiltonian to V_{N} expressed in terms of L and S is given by Abragam and Pryce[1] (see also ref. 8).

There is another cause of the interaction with nuclear spin, i.e., the electrostatic interaction with the electric quadrupole moment of the nucleus which is quadratic in **I**. It can be written

$$V_Q = [e^2Q/2I(2I - 1)]\sum_j[I(I + 1)/r_j^3 - 3(\mathbf{r}_j \cdot \mathbf{I})^2/r_j^5] \quad (24)$$

where Q is the quadrupole moment of the nucleus. A brief account of the derivation of this expression is given in Bleaney and Stevens' review article.[8]

Electron-spin resonance experiments are concerned with the transition between the lowest-lying levels of the paramagnetic ions in an external magnetic field. The analyses of the absorption spectra can be carried through by the use of the spin-Hamiltonian method developed by Pryce and his collaborators.[1,67] This useful method is applied to describe the complicated behavior of the levels lying lower than the microwave frequency by an effective Hamiltonian written in a compact form.

If there are $(2S' + 1)$ such Zeeman levels between which transitions are observed experimentally, we may confine ourselves to these levels and forget about the higher levels. Then we can describe the behaviors of the system in terms of $(2S' + 1) \times (2S' + 1)$ matrices. Thus one can represent the "effective" Hamiltonian of such a system as a function of the "fictitious spin" operator $\mathbf{S}'$ as well as the nuclear spin operator $\mathbf{I}$ if the nucleus of the magnetic ion has a spin $\mathbf{I}$. The symmetry of the crystalline field is reflected with fidelity by the effective spin-Hamiltonian, and the complicated effects of the various terms in the original Hamiltonian are involved in the coefficients, which are tensors in general, of the various terms of the spin-Hamiltonian. The detailed interpretation is, however, beyond the scope of this article, and the readers are referred to the review articles on the paramagnetic resonance.[8,50]

VI. INTERACTION WITH THE MOTION OF SURROUNDING NUCLEI

This section will be devoted to the interaction of the electrons in magnetic ion with the motion of the surrounding atoms. In many paramagnetic salts, each magnetic ion is surrounded by six negative ions or neutral molecules which are often called ligands. In such substances known as complex salts, the bonds between ligands and the metal ion are fairly strong, and we can treat the

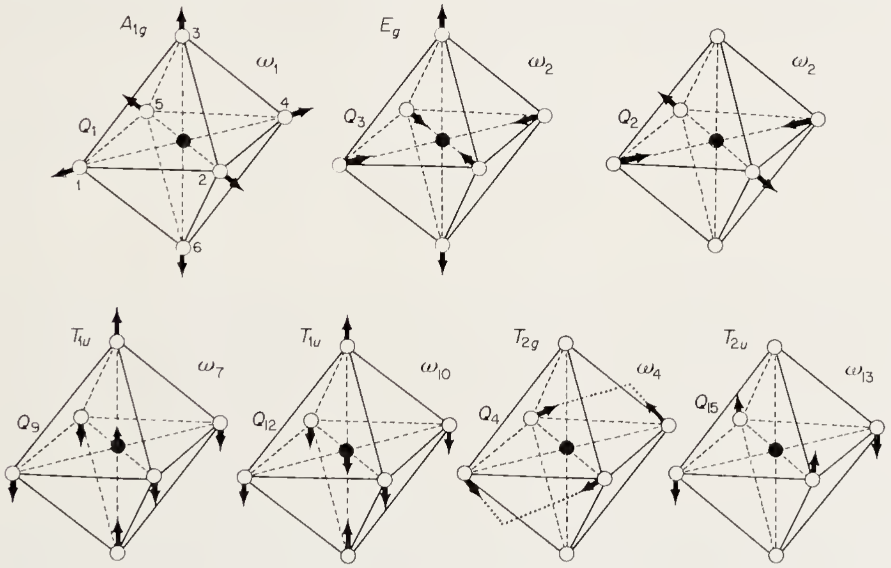

Fig. 4. Normal modes of an octahedral MX_6 molecule.

unit MX_6, X denoting ligand, as an isolated molecule to a good approximation. Actually, the bonds are not broken even in aqueous solution and the unit MX_6 exists as a so-called complex ion. In this section we shall treat the interaction of electrons of the metal ion with the molecular vibrations of the complex.

If we regard the ligands as mass points, there are six kinds of normal modes:[23,97] A_{1g}, E_g, $T_{1u}^{(1)}$, $T_{1u}^{(2)}$, T_{2g}, and T_{2u}. The normal coordinates of the two modes with T_{1u} symmetry depend upon the nature of the force between the atoms under consideration. The others can be determined geometrically from the symmetry irrespective of the force.

A. Intensity Caused by the Odd Vibrations

Electric dipole transition can take place only between the states of different parities. In the free ion, therefore, direct inner shell transitions as $d \rightarrow d$ and $f \rightarrow f$ are forbidden. For the ions in crystals, however, this prohibition is removed by the mixing of orbitals having opposite parity. Such mixing may be induced by (*a*) absence of a center of symmetry of the crystal field (existence of the hemihedral part of the crystal field) and (*b*) destruction of the center of symmetry by odd vibrations. This was first pointed out by Van Vleck.[96] In most salts of the $3d$ group ions the mechanism (*b*) plays the dominant role for the optical absorptions caused by the transitions between d^n states.[10]

The perturbation responsible for the mixing of the states having different parity (odd in the case of d^n configurations) is given by

$$H' = \sum_{Q} (\partial V/\partial Q)_{Q=0} Q \tag{25}$$

where Q's stand for the normal coordinates of the odd parity and V is the crystalline field acting on the $3d$ electrons. In order to know the explicit form of this expression, we have to know the normal coordinates Q's and the dependence of the crystalline field on them. Several assumptions on the forces between the constituent atoms in MX_6 are needed for the former purpose and one is obliged to adopt some special model, say point dipole model, for the calculation of the quantity $(\partial V/\partial Q)$. Another difficulty lies in that we know very little about the states with odd parity.

As a conventional approximation, we replace the energy denominators (i.e., the energy differences between the unperturbed states) by their appropriate mean value, and simplify the sum over the odd intermediate states by making use of the closure properties of the eigenfunctions. Furthermore, the matrix elements of $(\partial V/\partial Q)$ depend upon the values of $\langle r^n \rangle$, the determination of which is not easy in the present stage.

As a simple illustrative example, let us consider a linear molecule of XMX type. If we disregard the bending motion, there can be two normal vibrations, one being even and the other odd. The normal coordinates are

$$\begin{aligned} Q_{\text{even}} &= (x_1 - x_2)/\sqrt{2} \\ Q_{\text{odd}} &= [2x_0 - x_1 - x_2]/(2\gamma + 4\gamma^{-1})^{\frac{1}{2}} \end{aligned} \tag{26}$$

where γ is the ratio of the mass of M to that of X. If we adopt the point charge model, simple calculation shows

$$\begin{aligned} v_{\text{odd}} &= (\partial V/\partial Q_{\text{odd}})_{Q=0} \\ &= -(4Ze^2/R^2)(\gamma/2 + 1/\gamma)^{\frac{1}{2}} \sum_{m=0}^{\infty} (m+1)(r/R)^{2m+1} P_{2m+1}(\cos\vartheta) \end{aligned} \tag{27}$$

where we have assumed the charge of X as $-Ze$. According to the usual perturbation procedure, the matrix element of the transition dipole $\boldsymbol{P}$ between two states $|a;n\rangle$ and $|b;n'\rangle$ is given by the following expression:

$$\begin{aligned} \langle a;n|\boldsymbol{P}|b;n \pm 1\rangle &= \sum_i \langle a_0;n|v_{\text{odd}}Q_{\text{odd}}|i;n \pm 1\rangle\langle i;n \pm 1|\boldsymbol{P}|b_0;n \pm 1\rangle/(E_i - E_a) \\ &\quad + \sum_i \langle a_0;n|\boldsymbol{P}|i;n\rangle\langle i;n|v_{\text{odd}}Q_{\text{odd}}|b_0;n \pm 1\rangle/(E_i - E_b) \end{aligned} \tag{28}$$

where $|a_0\rangle$ and $|b_0\rangle$ are the unperturbed states corresponding to $|a\rangle$ and $|b\rangle$, respectively, and $|i\rangle$ stands for the excited states having different symmetry. In deriving this expression, use has been made of the fact that the matrix element of Q between two vibrational states does not vanish only when the quantum numbers differ by one from each other.

Only a few calculations have been performed in the quantitative estimates of the intensities so far, because of the difficulties mentioned above.[37,39,47,71] By the same reason, no general criterion has been obtained for the relative intensities of the various lines or bands.

The approximation of the nearly independent unit MX_6 is not valid in many compounds.[64] For such substances different approach should be required with respect to the treatment of the normal modes in crystal.

B. Band Width due to the Excitation of Even Vibrations

In the diagram of energy levels versus crystalline field strength parameter Δ, whereas the curves corresponding to the states having the same configuration $d\varepsilon^n d\gamma^{N-n}$ are parallel to each other, those of the different configurations have different slopes (see Fig. 3). If, therefore, we plot the adiabatic potential curves taking the MX distance as abscissa, the states having different configurations must have their energy minima at different MX distances. This means that such states have different equilibrium MX distances. When the complex undergoes an electronic transition between states with different equilibrium internuclear distances, it gives rise to the change in vibrational quantum numbers. Calculation based on the Franck–Condon principle confirms the possibility of any number of changes so that the consequent spectrum shows the vibrational structure or becomes a broad band. This can well account for the coexistence of broad bands and sharp lines experimentally found in the optical absorption spectra.[86]

The above discussion is valid only for the breathing mode of the A_{1g} symmetry. Since the adiabatic potentials depend on all the normal coordinates in general, the other modes will also contribute to the band width though they are of minor importance in many cases compared with the totally symmetric mode.

We shall first consider the case of transition between nondegenerate electronic states. Let the vibrational Hamiltonian before and after the transition be denoted by H_a and H_b, respectively. Then the absorption curve is given by the Fourier transform of the following function:[46]

$$I_{ba}(t) = \frac{\exp[-iE_0t/\hbar]\,\mathrm{Tr}\,[\exp(-H_a/kT)M_{ba}^{\star}\exp(iH_bt/\hbar)M_{ba}\exp(-iH_at/\hbar)]}{\mathrm{Tr}\,[\exp(-H_a/kT)]} \qquad (29)$$

where E_0 denotes the distance between two energy minima, M the transition moment, and the trace should be taken over the vibrational states. The calculation gives the absorption curve in a closed form when there is no frequency change.[5,25,38,61,99]

C. Jahn–Teller Effect

In relation to the above, a brief account will be given here of the Jahn–Teller effect.[59,86,97] When the electronic level of a molecule is degenerate at a structure of high symmetry, this structure is generally unstable and nuclear displacement may remove the degeneracy to stabilize the system. Distortion due to the effect will take place as the result of the terms of the vibrational Hamiltonian linear in the normal coordinates.

$$H_v = \sum_i [\tfrac{1}{2}(P_i^2 + \alpha_i Q_i^2) + v_i Q_i] \tag{30}$$

When the electronic state under consideration has an n-fold degeneracy, the coefficients v are expressed by $n \times n$ matrices as far as the mixing of the states in other levels is ignored.

As a simplest example, we shall again invoke the linear three atomic molecule XMX.[59] Suppose the two states denoted by $|s\rangle$ and $|a\rangle$ are nearly degenerate. If these states have different parity, say $|s\rangle$ being symmetric and $|a\rangle$ antisymmetric, then they will couple via the perturbation term $v_{\mathrm{odd}}\, Q_{\mathrm{odd}}$. In the static approximation, we regard the normal coordinate Q_{odd} as a parameter. Then we get a secular matrix of the Hamiltonian in the form

$$H_{\mathrm{electronic}} + (\alpha/2)Q_{\mathrm{odd}}^2 + H' = \begin{bmatrix} J + \alpha Q_{\mathrm{odd}}^2/2 & AQ_{\mathrm{odd}} \\ AQ_{\mathrm{odd}} & -J + \alpha Q_{\mathrm{odd}}^2/2 \end{bmatrix} \tag{31}$$

where $A = \langle s|v_{\mathrm{odd}}|a\rangle$, and $\alpha Q_{\mathrm{odd}}^2/2$ is the elastic potential term arising from forces between the atoms. Eigenvalues of the above secular matrix are readily obtained as

$$\alpha Q_{\mathrm{odd}}^2/2 \pm (J^2 + A^2 Q_{\mathrm{odd}}^2)^{\frac{1}{2}} \tag{32}$$

As is easily seen, the lower level has either two minima or one minimum at $Q_{\mathrm{odd}} = 0$ according as

$$|J| \lessgtr A^2/\alpha \tag{33}$$

In the former case, the stable configuration is unsymmetrical and the molecule shows Jahn–Teller distortion.

When we disregard the kinetic energy terms, we can determine the stable configurations of the system just by finding the minima of the potential energy as shown above. If, however, we take account of the kinetic energy terms, the problem becomes quite complicated as a consequence of a special coupling between vibrational modes and the electronic motion.[48,49,53] It seems to be impossible to get the answer of this dynamical Jahn–Teller problem in analytical forms. The dynamical effect would give rise to the complicated vibrational structure in the electronic transition spectra. This may be treated in principle by virtue of the expression (29) provided the coefficients in the vibrational Hamiltonians are properly chosen matrices. An interesting numerical calculation has been performed by Longuett-Higgins *et al.*[49] concerning the transition between nondegenerate and doubly degenerate electronic states. No experimental data undoubtedly attributable to this effect seems to be available at present.

Several evidences of the Jahn–Teller effect have been found in the paramagnetic resonance data, for which the readers are referred to the review article by Low.[50] Crystal distortion in magnetic compounds is also discussed by several authors. The most complete theoretical work may be that by Kanamori.[31]

VII. COVALENCY EFFECTS

The simplest crystal field theory deals with a purely atomic ion in a static electric field. This ionic model should, however, be regarded as an approximation to the real cases in which there can generally be certain amount of covalency in the bonding between the metal ions and the surrounding anions. The reduction of the Coulomb repulsion energy, expressed by the parameters B and C, and of the spin–orbit interaction constant λ implies the wider spread of the orbital functions than the purely atomic d functions[7,22,63,85] (see also Table XXII of ref. 50). The most direct experimental evidence for this covalency is the hyperfine structure due to anion nuclei observed in the electron spin resonance spectra by the metal ions. This phenomenon will be discussed in detail in the next section.

This covalency effect is taken care of by considering proper molecular orbitals spread out to the adjacent anions instead of purely atomic d orbitals. According to this picture, the d-orbital functions are augmented with small amounts of admixed anion orbitals of proper symmetry to form antibonding molecular orbitals, while the anion orbital functions are similarly augmented with d functions to form bonding orbitals. The bonding orbitals are filled with paired electrons and the unpaired antibonding electrons correspond to the incomplete d-shell electrons in the ionic model. A merit of Tanabe–Sugano's strong field scheme discussed in Section IV is that the theory can be applied to the present case by replacing the $d\varepsilon$ and $d\gamma$ orbitals by the corresponding proper molecular orbitals t_{2g} and e_g having T_{2g} and E_g symmetries, respectively. The parameter Δ or $10Dq$ is now regarded as the separation between these two one-electron levels.*

According to the symmetries, the $d\gamma$ orbits are combined with $2s$, $3s$, $2p_\sigma$, $3p_\sigma$ functions to make up σ bonds, and the $d\varepsilon$ orbits couple with p_π functions to form π bonds. Let the orbital functions of the surrounding ions be represented by $\psi_1, \psi_2, \ldots, \psi_6$, where the subscripts 1, 2, 3, 4, 5, and 6 denote atoms lying along the positive and negative x, y, and z axes of the octahedron. Then one can express the antibonding molecular orbitals by the following linear combinations[63,85]

$$\begin{aligned}
u &= N_\sigma[d\gamma(3z^2 - r^2) - \lambda_\sigma(2\psi_{\sigma 3} + 2\psi_{\sigma 6} + \psi_{\sigma 1} - \psi_{\sigma 4} + \psi_{\sigma 2} - \psi_{\sigma 5})/\sqrt{12}] \\
v &= N_\sigma[d\gamma(x^2 - y^2) - \lambda_\sigma(\psi_{\sigma 2} + \psi_{\sigma 4} - \psi_{\sigma 1} - \psi_{\sigma 5})/2] \qquad (34) \\
\xi &= N_\pi[d\varepsilon(yz) - \lambda_\pi(\psi_{\pi 2} - \psi_{\pi 5} + \psi_{\pi 3} - \psi_{\pi 6})/2]
\end{aligned}$$

Since the overlap between $d\varepsilon$ and p_π orbitals is much smaller than that between $d\gamma$ and s or p_σ functions, the covalency character, measured by the above parameters λ_π and λ_σ, is much weaker for t_{2g} orbitals than for the e_g orbitals, i.e., $\lambda_\pi < \lambda_\sigma$.

As the result of the covalent bonding, each of the electrons of a magnetic ion spends a part of the time in the neighboring anion orbits. However, this statement should not be accepted literally.

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* Because of the different degrees of covalency for t_{2g} and e_g orbitals, the same parameters B and C should not be used commonly for various configurations.[39] In this respect, a discussion is made by Tanabe in his recent paper.[87]

The same situation can be expressed in a different manner from a different point of view. Actually, migration of the anion electrons to the neighboring magnetic ions seems to be more probable than the reverse one. In fact, most of the theories on the superexchange interaction in antiferromagnetic compounds, which will be discussed in the following sections, are based on the mechanism in which virtual excited states expressing the latter type of electron transfer play essential roles in the spin coupling between magnetic ions through intervening anions.

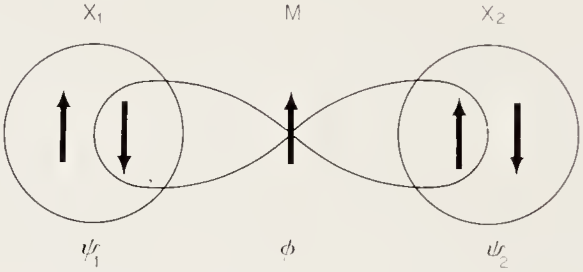

Fig. 5. Schematic diagram of the orbitals of the MX_2 unit.

In order to clarify the situation by a simplified model, we shall consider a three-center five-electron system of linear XMX type, where X stands for the anion and M the central metal ion. The equivalent one-electron orbital functions in the two anions will be denoted by ψ_1 and ψ_2, respectively. In the ionic approximation each of these is occupied by a pair of electrons. The representative orbital of the central magnetic ion will be expressed by ϕ which is occupied by an electron in the ionic case. The two anion functions ψ_1 and ψ_2 may be assumed orthogonal to each other because of the negligibly small overlap between them. But the orbital ϕ will not be orthogonal to ψ's.

$$\langle\psi_1|\psi_2\rangle = 0 \qquad S_1 = \langle\psi_1|\phi\rangle = \langle\psi_2|\phi\rangle \neq 0 \tag{35}$$

In the molecular orbital theory, the following two linear combinations are more conveniently used than the atomic orbitals ψ_1 and ψ_2.

$$\psi_+ = (\psi_1 + \psi_2)/\sqrt{2} \qquad \psi_- = (\psi_1 - \psi_2)/\sqrt{2} \tag{36}$$

Then

$$\langle\psi_-|\phi\rangle = 0 \qquad S = \langle\psi_+|\phi\rangle = \sqrt{2}\,S_1 \tag{37}$$

Hence only the ψ_+ function can be used to construct the required molecular orbital with ϕ. Before doing it, we shall first orthogonalize the orbitals in the manifold spanned by the three vectors ψ_1, ψ_2, and ϕ (or by ψ_+, ψ_-, and ϕ). If we fix ψ_1 and ψ_2, then we get the orthogonalized cation function ϕ_0 in the following form;

$$\phi_0 = (\phi - S\psi_+)/(1 - S^2)^{\frac{1}{2}} \tag{38}$$

Now the antibonding orbital will be introduced in the form:

$$\phi' = \cos\vartheta\,\phi_0 - \sin\vartheta\,\psi_+ \tag{39}$$

Then the bonding orbital should be given by

$$\psi'_+ = \sin\vartheta\,\phi_0 + \cos\vartheta\,\psi_+$$

Thus the total five-electron system will be specified by the configuration $(\phi')^1(\psi'_+)^2(\psi_-)^2$. However, the bonding and the nonbonding functions ψ'_+ and ψ_- are not very appropriate for describing

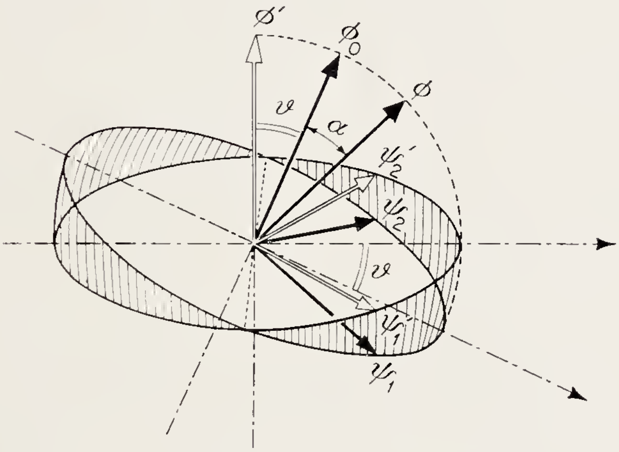

Fig. 6. Relative orientation of the orbitals represented by vectors.

the real electron orbitals because of their extraordinary spread with hollows at the centers. Instead of these, we should rather use the following functions, each of which is very similar to the original ψ's (Fig. 6).

$$\begin{aligned} \psi'_1 &= \tfrac{1}{2}(1 + \cos\vartheta)\psi_1 - \tfrac{1}{2}(1 - \cos\vartheta)\psi_2 + \sin\vartheta\,\phi_0/\sqrt{2} \\ \psi'_2 &= \tfrac{1}{2}(1 + \cos\vartheta)\psi_2 - \tfrac{1}{2}(1 - \cos\vartheta)\psi_1 + \sin\vartheta\,\phi_0/\sqrt{2} \end{aligned} \tag{40}$$

By using the properties of the determinantal functions, we can easily prove the relationship

$$(\phi')^1(\psi'_+)^2(\psi_-)^2 \equiv (\phi')^1(\psi'_1)^2(\psi'_2)^2$$

The explicit form of the wave function expressing the purely ionic state is given by the determinantal function

$$\Psi_{\mathrm{ionic}} \equiv [\psi_1\bar{\psi}_1\phi\psi_2\bar{\psi}_2]/(1-S^2)^{\frac{1}{2}}$$

where the term in brackets represents the usual Slater determinants multiplied by $(5\,!)^{-\frac{1}{2}}$. The orbitals without bar include up (α) spin and with bar down (β) spin functions respectively. Normalization factor $(1-S^2)^{-\frac{1}{2}}$ is necessary because of the non-orthogonality between ϕ and ψ's.

It is easily seen that the above function can be expressed in simpler form by using orthogonalized function defined above as

$$\Psi_{\mathrm{ionic}} = [\psi_1\bar{\psi}_1\phi\psi_2\bar{\psi}_2]/(1-S^2)^{\frac{1}{2}} = [\psi_1\bar{\psi}_1\phi_0\psi_2\bar{\psi}_2] \tag{41}$$

Now, let us take account of the covalency. The wave function will be given by

$$\Psi_{\mathrm{cov}} = [\psi'_1\bar{\psi}'_1\phi'\psi'_2\bar{\psi}'_2] \tag{42}$$

If we express this function in terms of the original atomic orbital functions, we get

$$\begin{aligned}\Psi_{\mathrm{cov}} &= \cos\vartheta[\psi_1\bar{\psi}_1\phi_0\psi_2\bar{\psi}_2] \\ &\qquad + (\sin\vartheta/\sqrt{2})\{[\psi_1\bar{\psi}_1\phi_0\psi_2\phi_0] + [\psi_1\bar{\phi}_0\phi_0\psi_2\bar{\psi}_2]\} \\ &= \{[(1-S^2)^{\frac{1}{2}}\cos\vartheta - S\sin\vartheta]/(1-S^2)\}[\psi_1\bar{\psi}_1\phi\psi_2\bar{\psi}_2] \\ &\qquad + [\sin\vartheta/\sqrt{2}\,(1-S^2)]\{[\psi_1\bar{\psi}_1\phi\psi_2\bar{\phi}] + [\psi_1\bar{\phi}\phi\psi_2\bar{\psi}_2]\}\end{aligned} \tag{43}$$

The first term of each expression represents the ionic state Ψ_{ionic}, and the rest the admixed excited configurations obtained by the electron transfer from one of the anions to the central magnetic ion. Thus we know that the partly covalent bonding between magnetic cation and the environments, which is usually described by proper molecular orbitals of the relevant electrons, is equivalent to the partial migration of the anion electrons in filled orbitals to the incomplete shells of the adjacent magnetic ions.

VIII. SUPER-HYPERFINE COUPLING

The direct experimental evidence for the covalency is the hyperfine structure of the paramagnetic resonance spectra of Mn^{2+} ions present substitutionally in a ZnF_2 crystal observed by Tinkham.[58,92] This is due to the hyperfine coupling of the electrons in the antibonding molecular orbitals with the surrounding six fluorine nuclei.[11] We shall tentatively call it "super-hyperfine" coupling. Shulman and Jaccarino[78] have succeeded in measuring the nuclear F^{19} resonance in a single crystal of MnF_2, and they found that the resonance pattern was shifted from the free-ion F^- value by a surprisingly large internal field. This can also be attributed to the super-hyperfine interaction.

For simplicity, we shall confine our attention to an Mn—F bond, and consider the effect between two $2s$ electrons in the F^- ion and one $3d\gamma$ electron in the Mn^{2+} ion. Let us denote the Hartree–Fock orbitals of the $2s$ and $3d\gamma$ electrons by ψ_s and ϕ_d, respectively. The overlap integral is defined by

$$S = \langle\psi_s|\phi_d\rangle = \int \psi_s^{\star}(\mathbf{r})\phi_d(\mathbf{r})d\mathbf{r} \tag{44}$$

Molecular orbital functions given by the linear combination of ψ_s and ϕ_d are as follows:

Bonding orbital:

$$\left.\begin{aligned}\psi' &= (\psi_s + \lambda\phi_d)/(1 + \lambda^2 + 2\lambda S)^{\frac{1}{2}}\\ &\text{Antibonding orbital:}\\ \phi' &= (\phi_d - \lambda\psi_s)/(1 + \lambda^2 - 2\lambda S)^{\frac{1}{2}}\end{aligned}\right\} \tag{45}$$

Then the wave function of the bond is expressed by the following determinant:

$$\Psi = (\text{Normalization})[\psi'\bar{\psi}'\phi'] \tag{46}$$

Expressing this function in terms of the original atomic orbitals, we get

$$\Psi = (\text{Normalization})\{[\psi_s\bar{\psi}_s\phi_d] + \lambda[\psi_s\bar{\phi}_d\phi_d]\} \tag{47}$$

This can also be expressed in the single determinantal form as

$$\Psi = (\text{Normalization})[\psi_s\overline{(\psi_s + \lambda\phi_d)}\phi_d] \tag{48}$$

The first term of (47) is the ground state of the system in the simple ionic model, which we shall call A configuration, i.e.,

$(A) = (2s)^2(3d)$. The second term is the excited configuration involving electron transfer from fluorine to manganese, which will be denoted by B, i.e., $(B) = (2s)(3d)^2$. We note that only the fluorine electron of spin β can transfer to Mn. The parameter λ, which expresses the amount of mixing of the excited configuration, can be determined according to the variational principle so as to minimize the energy of the bond.

The same result will be obtained by using the atomic orbital point of view. We start with the two configurations (A) and (B). Let the wave functions for these be

$$\Psi_A = [\psi_s\bar{\psi}_s\phi_d]/(1 - S^2)^{\frac{1}{2}} \qquad \Psi_B = [\psi_s\bar{\phi}_d\phi_d]/(1 - S^2)^{\frac{1}{2}} \tag{49}$$

Because of the overlap between ψ_s and ϕ_d, these functions are not orthogonal. Neglecting terms higher than first order in the overlap S, we have

$$\int \Psi_A^{\star}\Psi_B d\tau = S \tag{50}$$

Thus the secular equation has the form

$$\begin{vmatrix} H_{AA} - W & H_{AB} - WS \\ H_{BA} - WS & H_{BB} - W \end{vmatrix} = 0 \tag{51}$$

To order S we may replace the W's in the off-diagonal elements by its zero-order value H_{AA}. Then the standard perturbation theory yields (47) as the first-order wave function, where

$$\lambda = -(H_{AB} - SH_{AA})/(H_{BB} - H_{AA}) \tag{52}$$

The fluorine nuclear resonance shift is produced by an imbalance of the probability densities in the spin states α and β at the fluorine nucleus. In order to determine this imbalance, we must calculate the probability density associated with our first-order wave function Ψ with λ defined by (52). That the orbitals used in Ψ are not orthogonal makes the calculation complicated. We can simplify it tremendously by transforming the orbitals into an orthogonal set. The orthonormal set can be obtained similarly as in Section VII, and we get

$$\begin{aligned} \phi_1 &= (\cos\vartheta\, \phi_d' - \sin\vartheta\, \psi_s) \\ \phi_2 &= (\sin\vartheta\, \phi_d' + \cos\vartheta\, \psi_s) \end{aligned} \tag{53}$$

where

$$\phi_d' = (\phi_d - S\psi_s)/(1 - S^2)^{\frac{1}{2}} \tag{54}$$

and ϑ is an arbitrary parameter introduced to include the variety of the orthonormal sets (Fig. 7). Then Ψ becomes

$$\Psi = [\phi_1\overline{(\psi_s + \lambda\phi_d)}\phi_2]/(1 + \lambda^2 + 2S\lambda)^{\frac{1}{2}} = [\phi_1\bar{\psi}'\phi_2] \tag{55}$$

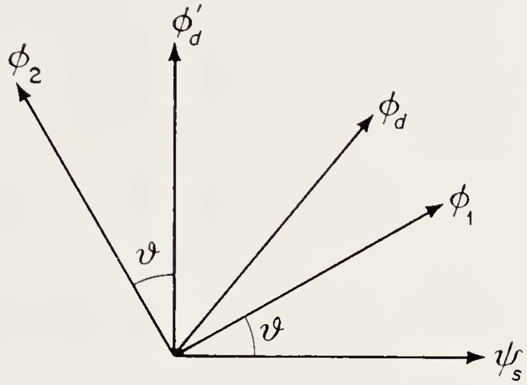

Fig. 7. Relative orientation of the orbitals associated with the Mn—F bond.

The probability density of α spin electrons is given by

$$\begin{aligned}(\text{P.D.})_\alpha &= |\phi_1|^2 + |\phi_2|^2 \\ &= (|\psi_s|^2 - 2S|\psi_s\phi_d| + |\phi_d|^2)/(1 - S^2) \\ &\fallingdotseq (1 + S^2)|\psi_s|^2 - 2S|\psi_s\phi_d| + (1 + S^2)|\phi_d|^2\end{aligned} \tag{56}$$

and similarly the probability density of β spin electrons is

$$\begin{aligned}(\text{P.D.})_\beta &= |\psi'|^2 \\ &= (|\psi_s|^2 + 2\lambda|\psi_s\phi_d| + \lambda^2|\phi_d|^2)/(1 + 2\lambda S + \lambda^2) \\ &\fallingdotseq (1 - \lambda^2 - 2\lambda S)|\psi_s|^2 + 2\lambda|\psi_s\phi_d| + \lambda^2|\phi_d|^2\end{aligned} \tag{57}$$

It should be noted that ϑ does not appear at all in (56) and (57). This means that we can use any orthonormal set. The expansion in these equations is to second order in λ and S. It is to be understood that ψ_s has argument $(\mathbf{r})$ whereas ϕ_d has $(\mathbf{r} - \mathbf{a})$, where $\mathbf{a}$ is the distance between the centers of the two ions.

We shall be interested in the difference,

$$(\text{P.D.})_\alpha - (\text{P.D.})_\beta = |(1 + S^2/2 - \lambda^2/2)\phi_d - (S + \lambda)\psi_s|^2 \tag{58}$$

This may be thought of as the probability density of the augmented manganese function,

$$\phi_d' = (1 + S^2/2 - \lambda^2/2)\phi_d - (S + \lambda)\psi_s \tag{59}$$

This function is even correctly normalized through second order. This is the antibonding molecular orbital, but we now see how it naturally arises from the total solution of the problem. If only S is taken account of, (59) reduces to (54), which is the approximation of Mukherji and Das.[55]

The isotropic shift of the fluorine resonance is given by the fractional probability charge evaluated at the fluorine nucleus contact interaction given by (19). This is

$$f = \left[\frac{(\text{P.D.})_\alpha - (\text{P.D.})_\beta}{(\text{P.D.})_\beta}\right]_{\text{nucleus}} = (S + \lambda)^2 \tag{60}$$

Here we have neglected $\phi_d(-\mathbf{a})$, that is, we assume that the charge density of the $3d$ electron is quite localized around the Mn nucleus.

According to the evaluation by Keffer *et al.*,[35]

$$S \simeq 0.05 \qquad \lambda \simeq 0.01 \tag{61}$$

Thus the isotropic shift is given by

$$f = (S + \lambda)^2 = 0.36 \times 10^{-2} \tag{62}$$

which is to be compared to the experimental value 0.50×10^{-2} by Shulman and Jaccarino.[78]

IX. DIRECT EXCHANGE INTERACTION

The $3d$ electrons in a magnetic compound crystal are localized about single ions, so that they can be described fairly adequately by the Heitler–London approach.[73] Usually, as explained in Section II, the orbital magnetic moment is quenched and only spin can contribute to the magnetic moment. When there are two magnetic ions with resultant spin $\mathbf{S}_i$ and $\mathbf{S}_j$ respectively at a reasonable distance from each other, we have the well-known magnetic dipolar interaction,

$$H_{\text{dip}} = (g^2\beta^2/r_{ij}^3)\{(\mathbf{S}_i \cdot \mathbf{S}_j) - 3(\mathbf{S}_i \cdot \mathbf{r}_{ij})(\mathbf{S}_j \cdot \mathbf{r}_{ij})/r_{ij}^2\} \tag{63}$$

Here $\mathbf{r}_{ij}$ is a radius vector connecting the ith and the jth ion, g the Landé g factor, β the Bohr magneton. The magnetic dipolar interaction is characteristic of long range and being anisotropic, but it is the weak interaction.

When nearest-neighbor electron wave functions overlap, we have the exchange interaction between them. We now consider a system[13] composed of N magnetic ions, each having one electron. The orbital wave functions are denoted by $\phi_1, \phi_2, \ldots, \phi_N$. They are all distinct from one another, because they belong to different ions. In this orbital configuration, we have 2^N different states, because the spin of each electron σ_i is either positive or negative. If we restrict our study to a manifold composed of these 2^N states, then the state can be specified by spin functions, and the Hamiltonian of the system can be replaced by the effective one operating only on spin functions. We denote any spin function by $\Theta_m(\sigma_1, \sigma_2, \ldots, \sigma_N)$, $m = 1, 2, \ldots, 2^N$. The antisymmetrized wave functions including both of the orbital and spin functions are

$$\Phi_m = (N!)^{-\frac{1}{2}} \sum_{\mathrm{P^t}} \delta_{\mathrm{P^t}} \mathrm{P^t} \phi_1(1)\phi_2(2) \ldots \phi_N(N) \times \Theta_m(\sigma_1, \sigma_2, \ldots, \sigma_N) \qquad (m = 1, 2, \ldots, 2^N) \tag{64}$$

where $\mathrm{P^t}$ is a permutation operator applying to the orbital and spin coordinates of the electrons, and $\delta_{\mathrm{P^t}}$ must have ± 1 according as $\mathrm{P^t}$ is an even or odd permutation.

The Hamiltonian of the system is a sum of Hamiltonian of single electron and Coulomb interactions between them as follows:

$$H = \sum_i H_i + \sum_{i>j} e^2/r_{ij} \tag{65}$$

Taking (64) as the basic functions, a matrix element of (65) is expressed by

$$H_{mm'} = \sum_\sigma \int \Phi_m^\star H \Phi_{m'} d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N \tag{66}$$

where $\sum_\sigma$ is the sum over spin variables, and the integrations over orbital coordinates. Now $\mathrm{P^t}$ can be factorized to a product of the permutation P applying to the orbital coordinates only and P^σ applying only to the spin coordinates, and we will define the following integral,

$$H_{\mathrm{P}} = \int \mathrm{P}\phi_1^\star(1) \ldots \phi_N^\star(N) H \phi_1(1) \ldots \phi_N(N) d\mathbf{r}_1 \ldots d\mathbf{r}_N \tag{67}$$

Then (66) would reduce to

$$H_{mm'} = \sum_{\mathrm{P}} \delta_{\mathrm{P}} H_{\mathrm{P}^{-1}} \sum_\sigma \Theta_m \mathrm{P}^\sigma \Theta_{m'} \tag{68}$$

We can easily understand from (68) that H is equivalent to

$$H = \sum_{\mathrm{P}} \delta_{\mathrm{P}} H_{\mathrm{P}^{-1}} \mathrm{P}^{\sigma} \tag{69}$$

operating on the spin functions. According to the Pauli principle, $\mathrm{PP}^{\sigma} = \delta_{\mathrm{P}}$, so that

$$\mathrm{P}^{\sigma} = \delta_{\mathrm{P}} \mathrm{P}^{-1} \tag{70}$$

Then we can write (69) as follows,

$$H = \sum_{\mathrm{P}} H_{\mathrm{P}} \mathrm{P} \tag{71}$$

To simplify the problem, we assume for the time being that all orbital functions ϕ_i are orthogonal. Then H_{P} is zero unless P is equal to the identity or the permutation P_{ij} consisting of the interchange of the orbital coordinates of the ith and jth electrons. Thus we have

$$H = H_{\mathrm{I}} - \sum_{i>j} J_{ij} \mathrm{P}^{\sigma}_{ij} \tag{72}$$

Here

$$J_{ij} = \int \phi_i^{\star}(j)\phi_j^{\star}(i)(e^2/r_{ij})\phi_i(i)\phi_j(j)d\mathbf{r}_i d\mathbf{r}_j \tag{73}$$

is called the exchange integral. If we denote + or − spin functions by α or β, respectively, we can express P^{σ}_{ij} using a complete set of spin functions for two electrons, $\alpha(i)\alpha(j)$, $\alpha(i)\beta(j)$, $\beta(i)\alpha(j)$, and $\beta(i)\beta(j)$;

$$\mathrm{P}^{\sigma}_{ij} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \tag{74}$$

On the other hand, the identity and $\mathbf{S}_i \cdot \mathbf{S}_j$ can be expressed by

$$1 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}, \qquad 4\mathbf{S}_i \cdot \mathbf{S}_j = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \tag{75}$$

Comparing (74) with (75), we get

$$\mathrm{P}^{\sigma}_{ij} = \tfrac{1}{2}(1 + 4\mathbf{S}_i \cdot \mathbf{S}_j) \tag{76}$$

Thus (72) would reduce to the familiar form of the spin Hamiltonian,

$$H = H_{\mathrm{I}} - \tfrac{1}{2} \sum_{i>j} J_{ij}(1 + 4\mathbf{S}_i \cdot \mathbf{S}_j) \tag{77}$$

Although we have used an approximation[82] that the orbital functions are orthogonal, we can discuss easily the simple case of two magnetic ions by the nonorthogonal orbital functions. In this case the Hamiltonian may be written

$$H = H_i + H_j + H' \tag{78}$$

where H_i amd H_j satisfy the following equations,

$$\begin{aligned} H_i\phi_i(1) &= [-(\hbar^2/2m)\Delta_1 - Ze^2/r_{i1}]\phi_i(1) = E_0\phi_i(1) \\ H_j\phi_j(2) &= [-(\hbar^2/2m)\Delta_2 - Ze^2/r_{j2}]\phi_j(2) = E_0\phi_j(2) \end{aligned} \tag{79}$$

That is, H_i (or H_j) is the Hamiltonian of the isolated ion i (or j), and E_0 is the eigenvalue, and Ze is the effective charge of the ion core. H' is the interactions,

$$H' = e^2/r_{12} - Ze^2/r_{i2} - Ze^2/r_{j1} \tag{80}$$

Here we have omitted the interaction between two ion cores, because it gives only an additive constant to the energy. The wave functions are those we put $N = 2$ in (64). Considering the nonorthogonality of the wave functions we obtain the following eigenvalue equation from (71),

$$\sum_{\mathrm{P}} (H_{\mathrm{P}} - W_{\mathrm{P}})\mathrm{P} = 0 \tag{81}$$

where W_{P} is

$$W_{\mathrm{P}} = W \int [\mathrm{P}\phi_i^\star(1)\phi_j^\star(2)]\phi_i(1)\phi_j(2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{82}$$

The permutation P contains only the identity and the single permutation P_{12}, so that (81) becomes

$$(2E_0 + C - W) + (2E_0S^2 + J - WS^2)\mathrm{P}_{12} = 0 \tag{83}$$

where

$$S = \int \phi_i^\star(1)\phi_j(1)d\mathbf{r}_1 \tag{84}$$

$$C = \int \phi_i^\star(1)\phi_j^\star(2)[e^2/r_{12} - Ze^2/r_{i2} - Ze^2/r_{j1}]\phi_i(1)\phi_j(2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{85}$$

$$J = \int \phi_i^\star(2)\phi_j^\star(1)[e^2/r_{12} - Ze^2/r_{i2} - Ze^2/r_{j1}]\phi_i(1)\phi_j(2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{86}$$

S is the overlap integral, C the Coulomb integral, J the exchange integral. Using (70) and (76), P_{12} may be written

$$\begin{aligned} \mathrm{P}_{12} &= -\tfrac{1}{2}(1 + 4\mathbf{S}_1 \cdot \mathbf{S}_2) \\ &= \begin{cases} -1 \text{ for triplet} & (\mathbf{S}_1 \text{ and } \mathbf{S}_2 \text{ are parallel}) \\ +1 \text{ for singlet} & (\mathbf{S}_1 \text{ and } \mathbf{S}_2 \text{ are antiparallel}) \end{cases} \end{aligned} \tag{87}$$

Thus we can obtain the following result from (83),

$$\begin{aligned} W &= 2E_0 + (C - J)/(1 - S^2) \qquad \text{for triplet} \\ W &= 2E_0 + (C + J)/(1 + S^2) \qquad \text{for singlet} \end{aligned} \tag{88}$$

Usually, S is so small compared to 1 that the triplet state or singlet state is stable according as J is positive or negative. As to the sign of J, if ϕ_i and ϕ_j are orthogonal, (86) is in agreement with (73) and J becomes positive. However, if ϕ_i and ϕ_j are the non-orthogonal s or p functions, J is negative and the absolute value $|J|$ is larger than (73). The accurate numerical calculations for d electrons are exceedingly difficult.[81] Kaplan[32] obtains a positive integral, but his results are inconclusive, because the accurate computations were not made at the internuclear distance appropriate to actual ferromagnetic material.

Serber[75] has extended Dirac's treatment to the case of many-orbital configurations. For ease in explanation, we will consider two configurations A and B. For the A configuration

$$\Phi^A = \phi_1(1)\phi_2(2)\ \ldots\ \phi_N(N) \tag{89}$$

and for the B configuration

$$\Phi^B = \phi_1'(1)\phi_2'(2)\ \ldots\ \phi_N'(N) \tag{90}$$

In each configuration, there are no identical orbitals, though ϕ_i and ϕ_i' may or may not be identical. In both configurations, we have the Hamiltonian according to (71) as follows,

$$H^{AA} = \sum_{\mathrm{P}} H_{\mathrm{P}}^{AA}\mathrm{P} \tag{91}$$

$$H^{BB} = \sum_{\mathrm{P}} H_{\mathrm{P}}^{BB}\mathrm{P} \tag{92}$$

If we make a complete one-to-one correspondence between ϕ_1 and ϕ_1', ϕ_2 and ϕ_2' etc., $\mathrm{P}\phi_1(1)\ \ldots\ \phi_N(N)$ would correspond to $\mathrm{P}\phi_1'(1)\ \ldots\ \phi_N'(N)$. Then P in (91) and (92) may be the same group of permutations for the two sets. Further we can write the Hamiltonian of interconfiguration using the same P as before,

$$H^{AB} = \sum_{\mathrm{P}} H_{\mathrm{P}}^{AB}\mathrm{P} \tag{93}$$

When the B configuration is (90) but the A configuration involves a pair of identical orbitals, say $\phi_1 = \phi_2$, (92) does not change, but in (91) we must strike out an element $\mathrm{P}_{12} = -1$, that is, we must eliminate the parallel spin state in two identical orbitals. By the same reason, in (93), we must strike out an element $\mathrm{P}_{12} = -1$ which operates on the A configuration and multiply a factor $\sqrt{2}$ in order to renormalize the whole energy matrix. Generally, if we have n and m pairs of identical orbitals in the A and B configurations, respectively, it is necessary to multiply a factor $\sqrt{2}^{|n-m|}$ to the interconfigurational portion. An application of Serber's treatment will be shown in the following sections.

X. SUPEREXCHANGE INTERACTION (I)

In a substance such as MnO, the magnetic ions are separated from each other by the intervening anion so that there is no direct exchange interaction between them. Shull *et al.*[77] have shown by neutron diffraction experiment on MnO that there exists a strong antiferromagnetic coupling between these magnetic ions. The mechanism of this coupling, which was first proposed by Kramers[45] and is called superexchange, will be discussed in this and the next sections.

Let us consider the system of two magnetic ions a and c, separated by an anion b. For simplicity we shall consider only two of the electrons on the anion b, assuming them to be in the same atomic orbital ψ_{b} with antiparallel spin state, and the magnetic ions a and c as possessing one electron each in the atomic orbitals ϕ_{a} and ϕ_{c} respectively, as shown in the following scheme:

Magnetic ion a	Anion b	Magnetic ion c
$\phi_{\mathrm{a}}(3)$	$\psi_{\mathrm{b}}(1)\psi_{\mathrm{b}}(2)$	$\phi_{\mathrm{c}}(4)$

This ground state is referred to as A configuration. In the present problem, P in (91) contains $4! = 24$ permutations, among which one set of twelve permutations P_{I}, P_{13}, P_{14}, P_{23}, P_{24}, P_{34}, P_{134}, P_{143}, P_{234}, P_{243}, $\mathrm{P}_{13.24}$, and $\mathrm{P}_{14.23}$ is independent. The members of this set are denoted by P. A second set of twelve elements can be obtained by operating P_{12} on those of P, i.e., $\mathrm{P}_{12}\mathrm{P}$. As $\psi_{\mathrm{b}}(1)$ and $\psi_{\mathrm{b}}(2)$ are the identical orbitals, P_{12} must be the identity. With this condition, the second set $\mathrm{P}_{12}\mathrm{P}$ simply repeats all the elements in P, and from (81) we have

$$(H - W)^{AA} = 2\sum_{\mathrm{P}}\delta_{\mathrm{P}}(H - W)^{AA}_{\mathrm{P}^{-1}}\mathrm{P}^{\sigma} = 0 \tag{94}$$

under the restriction $\mathrm{P}^{\sigma}_{12} = -1$. The overlap integrals will be given by

$$\int \phi^{\star}_{\mathrm{a}}(\mathbf{r})\phi_{\mathrm{e}}(\mathbf{r})d\mathbf{r} = 0 \tag{95}$$

$$S = \pm \int \psi^{\star}_{\mathrm{b}}(\mathbf{r})\phi_{\mathrm{a}}(\mathbf{r})d\mathbf{r} = \int \psi^{\star}_{\mathrm{b}}(\mathbf{r})\phi_{\mathrm{e}}(\mathbf{r})d\mathbf{r} \tag{96}$$

Here, and in the future, the top of the double sign is to be used if ψ_{b} is an even function such as *s* function, and the bottom when ψ_{b} is an odd function such as *p* function. Thus (94) becomes

$$\begin{aligned}(H^{AA}_{\mathrm{I}} - W) &- (H^{AA}_{13} - WS^2)(\mathrm{P}^{\sigma}_{13} + \mathrm{P}^{\sigma}_{23}) \\ &- (H^{AA}_{14} - WS^2)(\mathrm{P}^{\sigma}_{14} + \mathrm{P}^{\sigma}_{24}) + (H^{AA}_{13,24} - WS^4)(\mathrm{P}^{\sigma}_{13,24} + \mathrm{P}^{\sigma}_{14,23}) = 0\end{aligned} \tag{97}$$

In this equation H_{ij} is the shorthand for $H_{\mathrm{P}_{ij}}$.

Under the restriction $\mathrm{P}_{12} = -1$, we obtain from (76)

$$\mathrm{P}^{\sigma}_{13} + \mathrm{P}^{\sigma}_{23} = \mathrm{P}^{\sigma}_{14} + \mathrm{P}^{\sigma}_{24} = 1 \tag{98}$$

From this we also obtain

$$\begin{aligned}\mathrm{P}^{\sigma}_{13,24} + \mathrm{P}^{\sigma}_{14,23} &= (\mathrm{P}^{\sigma}_{13} + \mathrm{P}^{\sigma}_{23})(\mathrm{P}^{\sigma}_{14} + \mathrm{P}^{\sigma}_{24}) - \mathrm{P}^{\sigma}_{13}\mathrm{P}^{\sigma}_{14} - \mathrm{P}^{\sigma}_{23}\mathrm{P}^{\sigma}_{24} \\ &= 1 - \mathrm{P}^{\sigma}_{14}\mathrm{P}^{\sigma}_{34} - \mathrm{P}^{\sigma}_{24}\mathrm{P}^{\sigma}_{34} \\ &= 1 - \mathrm{P}^{\sigma}_{34}\end{aligned} \tag{99}$$

With the use of (98) and (99) one readily reduces (97) to

$$W = \frac{[H^{AA}_{\mathrm{I}} - (H^{AA}_{13} + H^{AA}_{14}) + H^{AA}_{13,24}(1 - \mathrm{P}^{\sigma}_{34})]}{[1 - 2S^2 + S^4(1 - \mathrm{P}^{\sigma}_{34})]} \tag{100}$$

To order S^4 the spin-dependent part of this energy is

$$W = -2\mathbf{S}_3 \cdot \mathbf{S}_4(H^{AA}_{13,24} - S^4 H^{AA}_1) = -2J_{\text{eff}}\mathbf{S}_3 \cdot \mathbf{S}_4 \qquad (101)$$

Here H^{AA}_{13} and H^{AA}_{14} have been dropped as being of order S^2 compared to H^{AA}_1. Equation (101) shows that there exists the same type of spin coupling between two magnetic ions as the direct exchange interaction. This coupling is the superexchange interaction. In (101) H^{AA}_1 is of order S^0, while $H^{AA}_{13,24}$ is of order S^4. Therefore J_{eff} is the quantity of order S^4, which fact was first pointed out by Yamashita and Kondo.[100]

We can easily understand by the following consideration that J_{eff} is negative and the order of S^4. By the overlap ϕ_a or ϕ_c is augmented proportionally to S onto the orbitals of the anion. Thus the mutual overlap by the modified orbitals of the two magnetic ions takes place. As the result of this overlap, we can expect the direct exchange between them. This exchange interaction favors the antiferromagnetic coupling, because the orbitals are nonorthogonal. As the amplitude of the wave function in the overlap region is proportional to S, the effective exchange integral J_{eff} is of order S^4.

Let us next consider the excited states. The excited configurations are those in which one electron is transferred from the anion to the magnetic ion c (B configuration) or to the magnetic ion a (C configuration). We restrict our calculation to the case in which the transferred electron occupies the same orbital as that of the electron already there. The orbitals in the three configurations A, B, and C will be shown according to the following scheme:

		Magnetic ion a	Anion b	Magnetic ion c
Configuration A	Φ^A	$\phi_a(3)$	$\psi_b(1)\psi_b(2)$	$\phi_c(4)$
Configuration B	Φ^B	$\phi_a(3)$	$\psi_b(4)$	$\phi_c(1)\phi_c(2)$
Configuration C	Φ^C	$\phi_a(1)\phi_a(2)$	$\psi_b(3)$	$\phi_c(4)$

For brevity, we neglect overlap of the functions except in so far as it is involved in the transfer and the exchange integrals, though the calculations due to Keffer and Oguchi[34] take account of all the overlap contributions arising from the interacting configurations.

With the labeling as the above, P_{12} will permute identical orbitals in all three configurations. Thus the entire secular equation will contain only the independent permutations P and no $\sqrt{2}$ factors are needed. The secular determinant is of the form

$$\begin{vmatrix} H_{\mathrm{I}}^{AA} - W & H_{14}^{AB}\mathrm{P}_{14} + H_{24}^{AB}\mathrm{P}_{24} & H_{13}^{AC}\mathrm{P}_{13} + \mathrm{H}_{23}^{AC}\mathrm{P}_{23} \\ H_{14}^{BA}\mathrm{P}_{14} + H_{24}^{BA}\mathrm{P}_{24} & H_{\mathrm{I}}^{BB} + H_{34}^{BB}\mathrm{P}_{34} - W & H_{13,24}^{BC}\mathrm{P}_{13,24} + H_{14,23}^{BC}\mathrm{P}_{14,23} \\ H_{13}^{CA}\mathrm{P}_{13} + H_{23}^{CA}\mathrm{P}_{23} & H_{13,24}^{CB}\mathrm{P}_{13,24} + H_{14,23}^{CB}\mathrm{P}_{14,23} & H_{I}^{CC} + H_{34}^{CC}\mathrm{P}_{34} - W \end{vmatrix} = 0 \tag{102}$$

Here

$$H_{\mathrm{I}}^{AA} = 0, \qquad H_{\mathrm{I}}^{BB} = H_{\mathrm{I}}^{CC} = \Delta E \tag{103}$$

$$H_{14}^{AB} = H_{24}^{AB} = b, \qquad H_{13}^{AC} = H_{23}^{AC} = \pm b \tag{104}$$

$$H_{34}^{BB} = H_{34}^{CC} = J, \qquad H_{13,24}^{BC} = H_{14,23}^{BC} = \pm J' \tag{105}$$

where ΔE is the excited energy, and

$$b = \int \psi_b^{\star}(1)H(1)\phi_c(1)d\mathbf{r}_1 \tag{106}$$

$$J = \int \psi_b^{\star}(1)\phi_c^{\star}(2)H(1{,}2)\phi_c(1)\psi_b(2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{107}$$

$$J' = \int \phi_a^{\star}(1)\psi_b^{\star}(2)H(1{,}2)\psi_b(1)\phi_c(2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{108}$$

In these b is the transfer integral, J the exchange integral and J' the exchange integral with three centers. Using (98) and (99), (102) may be simplified,

$$\begin{vmatrix} -W & -b & \mp b \\ -b & \Delta E + J\mathrm{P}_{34} - W & \pm J'(1 + \mathrm{P}_{34}) \\ \mp b & \pm J'(1 + \mathrm{P}_{34}) & \Delta E + J\mathrm{P}_{34} - W \end{vmatrix} = 0 \tag{109}$$

The A configuration is even with respect to the anion center. If we make the even and odd combinations of the excited configurations,

$$\Phi_{\mathrm{even}} = (\Phi^B \pm \Phi^C)/\sqrt{2} \tag{110}$$

$$\Phi_{\mathrm{odd}} = (\Phi^B \mp \Phi^C)/\sqrt{2} \tag{111}$$

then (109) may be reduced to the following simple form:

$$\begin{vmatrix} -W & -\sqrt{2}b & 0 \\ -\sqrt{2}b & \Delta E+J'+(J+J')\mathrm{P}_{34}-W & 0 \\ 0 & 0 & \Delta E-J'+(J-J')\mathrm{P}_{34}-W \end{vmatrix} = 0 \tag{112}$$

Thus the energy of the ground state depending on the spin orientation is given by

$$W = -[4b^2/(\Delta E)^2](J + J')(\mathbf{S}_3 \cdot \mathbf{S}_4) \tag{113}$$

The term of J is called the Anderson mechanism,[2,98] and that of J' the Anderson–Hasegawa mechanism.[56] Both of J and J' are negative, so that (113) gives antiferromagnetic coupling.

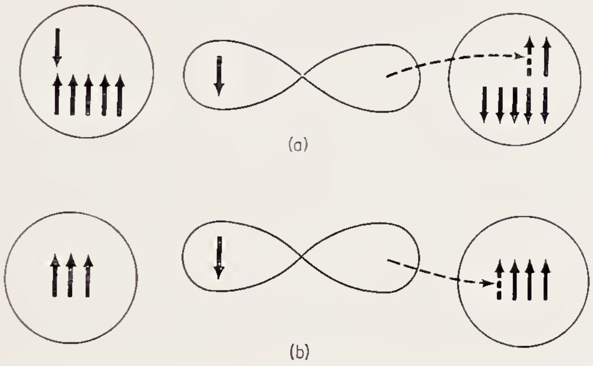

Fig. 8. Anderson's mechanism for the superexchange interaction: (a) more-than-half-filled case, (b) less-than-half-filled case.

We shall consider qualitatively the Anderson mechanism in the case of more than 5 electrons on the magnetic ion (more-than-half-filled case). As shown in Fig. 8(a), the electron on the anion must transfer to a half filled orbital and align its spin antiparallel to the net spin on the magnetic ion. The anion from which the electron is transferred has a net spin which is antiparallel to that of the removed electron. This net spin has antiferromagnetic coupling with that of the magnetic ion on the other side. Therefore, we have antiferromagnetic superexchange coupling between two magnetic ions. The quantitative calculation discussed above has been based on the simplified model in more-than-half-filled case.

On the other hand, if the number of the electrons on the magnetic ions is less than 4 (less-than-half-filled case), spin of the transferred electron is parallel to that of the magnetic ion due to Hund's rule. The result gives ferromagnetic superexchange coupling as is easily seen in Fig. 8(b).

In the Anderson–Hasegawa mechanism, which is shown in Fig. 9, the transferred electron to the right magnetic ion returns to the anion, simultaneously with the jump of the remaining electron from the anion to the left magnetic ion in the excited state. The result gives antiferromagnetic superexchange coupling irrespective of whether it is a more-than-or less-than-half-filled case.

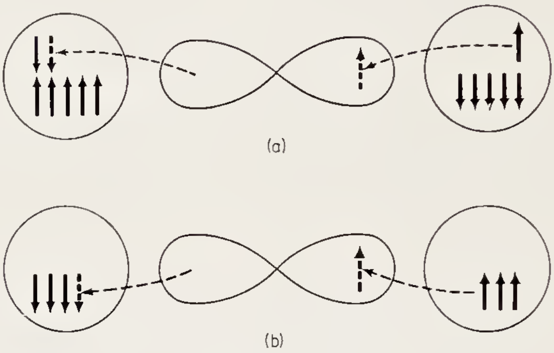

Fig. 9. Anderson-Hasegawa's mechanism for the superexchange interaction: (a) more-than-half-filled case, (b) less-than-half-filled case.

If the superexchange coupling occurs through *p* electrons on the anion, that is, if the electron making the transition to the magnetic ion is primarily *p* electron, the remaining *p* electron in the same state will provide the direct exchange coupling with the magnetic ion diametrically opposite the first magnetic ion. Thus we expect the strongest superexchange coupling in the case of two magnetic ions at opposite ends of an anion dumbbell *p* orbital, and this accounts for the next-nearest-neighbor antiferromagnetic ordering in MnO crystal.

XI. SUPEREXCHANGE INTERACTION (II)

Many different mechanisms have been proposed after Anderson.[40,41,57,66,76] According to Slater,[83] the potential energy of a plus-spin electron on an anion is different from that of a minus-spin electron in the identical orbital on account of the exchange effect with neighboring magnetic ions. Therefore the orbital of the plus-spin electron is modified so as to get closer to a magnetic ion with plus spin in order to gain the exchange energy. The orbital of the minus-spin electron is modified so as to get closer to a magnetic ion with minus spin on the opposite side of the anion. As a result, the anion is polarized. This mechanism can be effective only when the magnetic ions on both sides have antiparallel spin, so that it is antiferromagnetic coupling.

Similar polarization effect can occur if there is a covalent bonding between a magnetic ion and an anion. In this case, the polarization of an anion is just contrary to Slater's mechanism. However, it also gives rise to the antiferromagnetic superexchange coupling.

In the previous treatments, it was assumed that when the magnetic ion *d* shell is more than half filled, any additional electron will occupy a half filled *d* orbital and align its spin antiparallel to that existing on the magnetic ion. This prediction is based on the supposition that there are no unfilled orbitals available that are degenerate with the 3*d* orbitals. Goodenough and Loeb[20] have proposed that on a magnetic ion in a crystal, there may be empty hybridized orbitals of *d*, *s*, and *p*, whose energy is about the same as that of the filled or partially filled *d* orbitals, and that if an electron is transferred to the magnetic ion, it would produce parallel spin alignment to the net spin of the magnetic ion when this hybrid orbital is occupied. This means the exchange energy is gained if the anion electron with spin parallel to that of the magnetic ion is excited to become part of the magnetic ion. Since only one electron participates in this bond, the bond is called semi-covalent. If one of the anion electrons with plus spin participates in the semi-covalence with a magnetic ion, and the other electron with minus spin participates in semi-covalence with a magnetic ion on the other side of the anion, the spins of the two magnetic ions would be coupled antiparallel.

Kanamori[30] pointed out the importance of the symmetry of the transferred electron wave function in the crystalline field. When the crystalline field has cubic symmetry, the *d* orbitals are split into two sublevels denoted by $d\varepsilon$ and $d\gamma$ as explained in

Section IV. When the magnetic ion is surrounded octahedrally by the anions, the energy level of the $d\varepsilon$ orbitals is lower than that of $d\gamma$. We denote the p function of the anion which is extending towards the neighboring magnetic ion by ψ_σ, and those perpendicular to ψ_σ by ψ_π. As is easily seen in Fig. 10, ϕ_γ is orthogonal to ψ_π and ϕ_ε is orthogonal to ψ_σ. If two orbitals are orthogonal on account of the symmetry, there will be no electron transfer between these orbitals. Therefore, when two magnetic ions and the intervening anion lie in a row along z axis, nonvanishing transfer integrals are those between $\phi_\gamma(3z^2 - r^2)$ and ψ_σ, $\phi_\varepsilon(zx)$ and $\psi_\pi(x)$, and $\phi_\varepsilon(yz)$ and $\psi_\pi(y)$. On the other hand, exchange integrals are positive or negative according to whether the orbitals are orthogonal or not. For example, let us consider $CaMnO_3$ crystal. This is the pervoskite type and an Mn^{4+} ion is surrounded by six O^{2-} ions octahedrally. There are three $3d$ electrons on the Mn^{4+} ion, which fill $d\varepsilon$ levels just half aligning their spins parallel to each other. The ψ_σ electron as well as the s electron on the

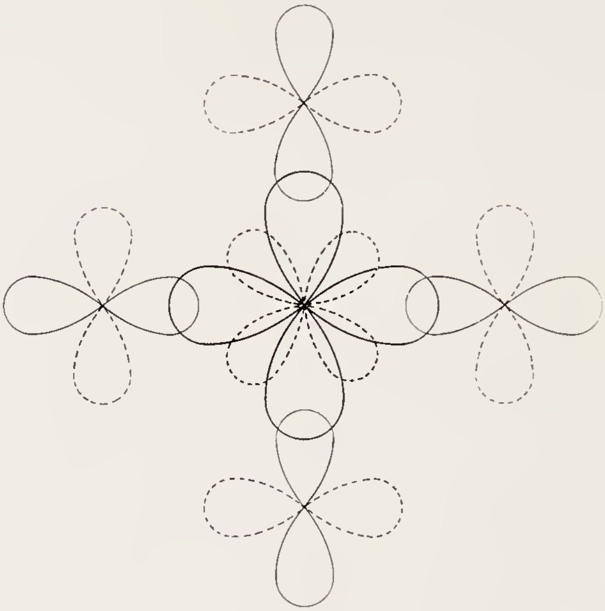

Fig. 10. The heavy full lines represent $\phi_\gamma(x^2 - y^2)$ orbital, and the heavy dashed lines $\phi_\xi(xy)$. The thin full lines represent ψ_σ, and the thin dashed lines ψ_π.

O^{2-} ion, whose spin is parallel to that of the Mn^{4+} ion, can transfer to the $d\gamma$ level. The remaining ψ_σ electron or s electron on the O^{2-} ion couples ferromagnetically with the three $d\varepsilon$ electrons on the Mn^{4+} ion located on the other side, because these wave functions are orthogonal to each other. We, therefore, obtain antiferromagnetic superexchange coupling between the two Mn^{4+} ions.

On the other hand, the ψ_π electron, whose spin is antiparallel to that of the Mn^{4+} ion, can transfer to the ϕ_ε orbital, because ϕ_ε orbitals are just half filled. The remaining ψ_π electron on the O^{2-} ion couples with one of three ϕ_ε electrons with the negative exchange integral, and also couples with other two ϕ_ε electrons with the positive exchange integral, but the latter exchange integrals are much smaller than the absolute value of the former exchange integral, so that the sum of the three exchange integrals is negative (antiferromagnetic coupling). After all, we have an antiferromagnetic superexchange coupling in this case, too. These predictions are in agreement with the experimental results.

This example shows that the antiferromagnetic superexchange coupling exists even in the less-than-half-filled case, contrary to Anderson's theoretical result, which predicts always ferromagnetic superexchange coupling in the less-than-half-filled case.

Recently Anderson[3] developed another theory of superexchange interaction. Following Anderson, we call a crystal from which all the d electrons are excluded a diamagnetic lattice. We assume the existence of an exact solution of the problem of a single d electron in the diamagnetic lattice. This solution, in principle, involves an antibonding admixture of anion function, so that we need not consider any additional electron transfer effect discussed above. This d electron is surrounded by an accompanying cloud of the electronic dielectric polarization. This dielectric polarization involves the spin-dependent polarization caused by the exchange effect as well as the ordinary spin-independent polarization. We denote the d electron carrying with it a cloud of the associated spin-dependent polarization by d' electron.

Inserting many d electrons into the diamagnetic lattice to complete the crystal, every d electron becomes a d' electron. They are repelled when they come too near each other. Whenever this repulsion predominates, the ground state will be that with some definite number of d' electrons on each magnetic ion; the perturbed virtual state that with one or more electrons transferred to other magnetic ions.

For brevity, let us consider the simple case of one d' electron per magnetic ion. Figure 11 shows the energy levels of any pair of two neighboring magnetic ions, M_1 and M_2. The level labeled by u is occupied by a single d' electron and the four levels labeled by v are empty. We assume these five levels are degenerate, though they are drawn separately in Fig. 11 in order to facilitate the understanding.

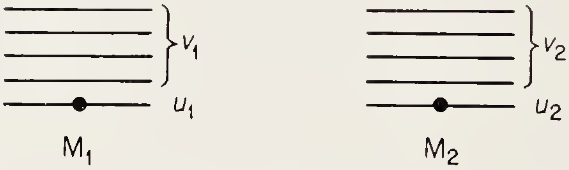

Fig. 11. Energy levels of a pair of two neighboring magnetic ions M_1 and M_2. Dots represent the d' electrons.

If the spins of the d_1' and d_2' electrons are antiparallel, the d_2' electron can transfer to any level of u_1 or v_1 in the excited states. The matrix element of the transition from u_2 to any one of v_1 is denoted by b', while that from u_2 to u_1 is $\sqrt{2}b$.[*] Thus the second-order perturbation of the energy is

$$E_{\mathrm{a}} = -6b'^2/U \tag{114}$$

[*] The matrix element expressing the transition of the d' electron from u_2 to any one of v_1 is

$$\sum_{\text{spin}} \iint (1/\sqrt{2})[u_1^\star(1)u_2^\star(2) + u_2^\star(1)u_1^\star(2)](1/\sqrt{2})[\alpha_1\beta_2 - \beta_1\alpha_2][H(1) + H(2)]$$
$$\times (1/\sqrt{2})[u_1(1)v_1(2) + v_1(1)u_1(2)](1/\sqrt{2})[\alpha_1\beta_2 - \beta_1\alpha_2]d\mathbf{r}_1 d\mathbf{r}_2 = b'$$

where

$$b' = \int u_2^\star(1)H(1)v_1(1)d\mathbf{r}_1,$$

while the matrix element from u_2 to u_1 is

$$\sum_{\text{spin}} \iint (1/\sqrt{2})[u_1^\star(1)u_2^\star(2) + u_2^\star(1)u_1^\star(2)](1/\sqrt{2})[\alpha_1\beta_2 - \beta_1\alpha_2][H(1) + H(2)]$$
$$\times u_1(1)u_1(2)(1/\sqrt{2})[\alpha_1\beta_2 - \beta_1\alpha_2]d\mathbf{r}_1 d\mathbf{r}_2 = \sqrt{2}b'$$

where

$$b' = \int u_2^\star(1)H(1)u_1(1)d\tau_1$$

assumed to be the same as the above b'.

where b' is the transfer integral of the d' electron from M_1 to M_2, U the energy of the excited state with one transferred d' electron.

On the contrary, if the spins of the d_1' and d_2' electrons are parallel, the transfer of the d_2' is restricted to any one of the four v_1 levels. The second-order perturbation of the energy is

$$E_{\mathrm{p}} = -4b'^2/(U-J) \fallingdotseq -4b'^2(1+J/U)/U \qquad (115)$$

where J is the intra-atomic exchange integral, which is always positive. The energy difference between antiparallel and parallel spin configurations is

$$W = 2(E_{\mathrm{a}} - E_{\mathrm{p}}) = 2[(2b'^2/U) - 4(b'^2J/U^2)](\mathbf{S}_{d_1'} \cdot \mathbf{S}_{d_2'}) \qquad (116)$$

Here the factor 2 has been employed, because the d_1' electron can give the same contribution by the transition to M_2 ion. The first term in the right-hand side of (116) is the antiferromagnetic coupling by the transition of the d_1' electron to the u level of the neighboring ion, and the second term is the ferromagnetic coupling by the transition to the v levels. The ferromagnetic term is less, by the order of J/U or about a factor 5–10, than the antiferromagnetic term. Therefore (116) gives the antiferromagnetic superexchange coupling as a whole. This result is in agreement with the experimental fact, which is that in almost all the known crystals except CrO_2[79] the dominant superexchange interaction is clearly antiferromagnetic.

Anderson further discusses the direct exchange interaction between d' electrons and an indirect exchange interaction through the spin polarization.

Moriya[54] derives the following anisotropic superexchange interaction by extending the Anderson theory to include the spin–orbit coupling,

$$W = \mathbf{D} \cdot [\mathbf{S}_{\mathrm{d}_1'} \times \mathbf{S}_{\mathrm{d}_2'}] \qquad (117)$$

where **D** is a constant vector. This interaction was first suggested in magnetic crystals of low symmetry such as α-Fe_2O_3 from purely symmetry ground by Dzyaloshinsky.[14]

XII. DOUBLE-EXCHANGE INTERACTION

In the mixed manganites of perovskite structure, such as $(Ba_xLa_{1-x})(Mn_x^{4+}Mn_{1-x}^{3+})O_3$, there appears ferromagnetism,[26] though pure $BaMnO_3$ or $LaMnO_3$ is not ferromagnetic. Zener[103] has proposed a new mechanism which he named double-exchange interaction in order to account for this ferromagnetism. In the above mixed crystal, we have a configuration of Mn^{3+} and Mn^{4+} ions intervening by O^{2-} ion. In a ground state A, an electron with plus spin can transfer from the O^{2-} ion to the right Mn^{4+} ion (excited state), and then a second electron with plus spin can transfer from the left Mn^{3+} ion to the O^{2-} ion. This is again a ground state, which is a different configuration from the ground state A, so that we denote it by a ground state B. Thus we have the resonance between two degenerate ground states A and B. This resonance will be greatest when the spins of both manganese ions are aligned parallel. Therefore, double-exchange interaction will lead to a ferromagnetic coupling.

Anderson and Hasegawa[4] have developed in detail a theory of double-exchange interaction, following the proposal by Zener. We shall here explain double-exchange interaction in a simple case, in which there are only two electrons on one magnetic ion, one on the other. The orbital configuration will be shown according to the following scheme:

	Magnetic ion M_1	Magnetic ion M_2
Configuration A	$\phi'_a(1)$	
	$\phi_a(2)$	$\phi_c(3)$
Configuration B		$\phi'_c(1)$
	$\phi_a(3)$	$\phi_c(2)$

Although the transfer mechanism between configurations A and B takes place via the O^{2-} ion, we will eliminate the electrons on the O^{2-} ion, instead of it, we will introduce the transfer integral b' between two magnetic ions, which is similar to that used in Anderson's new theory[3] of superexchange interaction explained in the previous section. On magnetic ion M_1 or M_2, we assume the spins of two electrons are aligned parallel (triplet) according to Hund's rule. The energy of the ground state is denoted by $E(t)$. We will neglect overlap effect except insofar as it is involved in transfer integral b', as before. The secular determinant will be of the form:

$$\begin{vmatrix} E(t) - W & H_{23}^{AB}P_{23} \\ H_{23}^{BA}P_{23} & E(t) - W \end{vmatrix} = 0 \qquad (118)$$

where

$$H_{23}^{BA} = b' \tag{119}$$

With the use of (70) and (76), one readily reduces (118) to

$$W = E(t) \pm b'\mathrm{P}_{23} = E(t) \mp b'[\tfrac{1}{2} + 2\mathbf{S}_2 \cdot \mathbf{S}_3] \tag{120}$$

Here $\mathbf{S}_i$ is the spin operator of the ith electron. We further introduce the spin operator defined by

$$\mathbf{S}_0 = \mathbf{S}_1 + \mathbf{S}_2 \tag{121}$$

In the ground triplet state, $\mathbf{S}_1 - \mathbf{S}_2 = 0$, so (120) may be written

$$\begin{aligned} W &= E(t) \mp b'[\tfrac{1}{2} + \mathbf{S}_0 \cdot \mathbf{S}_3 + (\mathbf{S}_2 - \mathbf{S}_1) \cdot \mathbf{S}_3] \\ &= E(t) \mp b'[\tfrac{1}{2} + \mathbf{S}_0 \cdot \mathbf{S}_3] \end{aligned} \tag{122}$$

We note that the expression of double-exchange interaction, which has the ± sign in (122), is different from those of direct exchange or superexchange interaction. Considering that $\mathbf{S}_0 \cdot \mathbf{S}_3$ is $\frac{1}{2}$ or -1 according to whether $\mathbf{S}_0$ and $\mathbf{S}_3$ are parallel, that is, $|\mathbf{S}_0 + \mathbf{S}_3| = 3/2$ (quartet), or antiparallel, that is, $|\mathbf{S}_0 + \mathbf{S}_3| = \frac{1}{2}$ (doublet), we have

$$W = E(t) \mp b' \qquad \text{(quartet)} \tag{123}$$

$$W = E(t) \pm (b'/2) \quad \text{(doublet)} \tag{124}$$

Equations (123) and (124) show that the average energy of the quartet state is the same as that of the doublet state. This suggests that the calculated susceptibility does not obey the Curie–Weiss law but approximately the Curie law far above the Curie temperature. But this prediction is not borne out in experiments.

XIII. INDIRECT-EXCHANGE INTERACTION

When the magnetic crystal has conduction electrons, there are exchange interactions between localized magnetic electrons, called *d* electrons, and conduction electrons, called *s* electrons. We shall call this exchange interaction *s–d* interaction. Since *s–d* interaction is ferromagnetic, the energy is gained if the spins of *s* and *d* electrons are polarized in the same direction. If, however, *s* electrons are filled in both spin states up to the Fermi surface, kinetic energy of the *s* electrons must be increased when minus-spin electrons change to plus-spin electrons. As the result of balancing of both energies, *s* electrons would be more or less polarized and simultaneously the spins of *d* electrons would be aligned parallel, in other words, *d* electrons would be coupled ferromagnetically with each other. This is called indirect-exchange coupling, first suggested by Zener.[102] The Zener mechanism, however, is too naive. According to Yosida[33,101] the Zener mechanism, which is due to the first-order perturbed energy, is completely modified by the first-order perturbation of the wave function of the *s* electrons, and therefore spin coupling between two *d* electrons is not always ferromagnetic but can also be antiferromagnetic.

We shall treat indirect exchange interaction using Ruderman–Kittel's method,[70] which is concerning the hyperfine interaction between *s* electrons and nuclei in metals. The result obtained by this method will be the same as that of Yosida's method.

The behaviors of an *s* electron may be adequately described by the Bloch function,

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp\,(i\mathbf{kr})u_{\mathbf{k}}(\mathbf{r}) \tag{125}$$

where $\mathbf{k}$ is the wave-number vector and $u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the lattice. It is normalized for the volume V of the crystal as follows,

$$V^{-1}\int \psi_{\mathbf{k}}^{\star}(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r})d\mathbf{r} = 1 \tag{126}$$

Considering the expression (93) for the configurational interaction explained at the end of Section IX, the matrix element for the scattering from $\mathbf{k}$ to $\mathbf{k}'$ by the exchange interaction with a *d* electron localized on the magnetic ion at $\mathbf{R}_l$ is

$$-(1/N)J(\mathbf{k},\mathbf{k}')\exp\,[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_l][1+4(\mathbf{s}\cdot\mathbf{S}_l)]/2 \tag{127}$$

Here $\mathbf{s}$ and $\mathbf{S}_l$ stand for the spin operators of the *s* electron and the *d* electron, respectively, and $J(\mathbf{k},\mathbf{k}')$ is the exchange integral defined by

$$\begin{aligned} J(\mathbf{k},\mathbf{k}') = N\int \exp\,[-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_l]\psi_{\mathbf{k}'}^{\star}(\mathbf{r}_1)\phi_d^{\star}(\mathbf{r}_2-\mathbf{R}_l)(e^2/r_{12}) \\ \times\,\psi_{\mathbf{k}}(\mathbf{r}_2)\phi_d(\mathbf{r}_1-\mathbf{R}_l)d\mathbf{r}_1d\mathbf{r}_2 \end{aligned} \tag{128}$$

where $\phi_d(\mathbf{r}-\mathbf{R}_l)$ is the Wannier function for the *d* electron. Keeping only terms involving the spins, we write instead of (127),

$$-(2/N)J(\mathbf{k},\mathbf{k}')\exp\,[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_l](\mathbf{s}\cdot\mathbf{S}_l) \tag{129}$$

The interaction (129) is so weak compared to the electron lattice coupling that it is sufficient to treat it as a small perturbation. Then the interaction between two d electrons at $\mathbf{R}_l$ and $\mathbf{R}_m$, respectively, may be given by the second-order perturbation theory as follows,

$$W(\mathbf{R}_{lm}) = -\sum_{\substack{s\text{-elect.}\\ \text{spin}}} (\mathbf{s}\cdot\mathbf{S}_l)(\mathbf{s}\cdot\mathbf{S}_m)(V^2/N^2)\int_0^{\mathbf{k}_m}(2\pi)^{-3}d\mathbf{k}\int_{\mathbf{k}_m}^{\infty}(2\pi)^{-3}d\mathbf{k}'$$
$$\times\, 4|J(\mathbf{k},\mathbf{k}')|^2\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{lm}]/[E(\mathbf{k}')-E(\mathbf{k})] + \text{c.c.} \quad (130)$$

where

$$\mathbf{R}_{lm} = \mathbf{R}_l - \mathbf{R}_m \quad (131)$$

and $\mathbf{k}_m$ is the wave-number vector at the Fermi surface, and $E(\mathbf{k})$ is the energy of the s electron having the wave number $\mathbf{k}$. In (130) the transition to the intermediate excited state is due to the d electron at $\mathbf{R}_l$ and the wave number vector of the s electron changes from $\mathbf{k}$ to $\mathbf{k}'$; on the other hand, the transition back to the ground state is due to the d electron at $\mathbf{R}_m$ with simultaneous change from $\mathbf{k}'$ to $\mathbf{k}$, or the role of the both d electrons is reversed, and the restriction $|\mathbf{k}'| > |\mathbf{k}_m|$ is dictated by the Pauli principle. We assume the quantity $J(\mathbf{k},\mathbf{k}')$ does not depend strongly on $\mathbf{k}$ and $\mathbf{k}'$. Since the largest contributions to (130) come when $\mathbf{k}$ and $\mathbf{k}'$ are nearly equal to $|\mathbf{k}_m|$ we may approximate $|J(\mathbf{k},\mathbf{k}')|^2$ by $|J(\mathbf{k}_m,\mathbf{k}_m)|^2$. If it is assumed that the effective mass $m^\star$ of the s electron does not vary appreciably for $|\mathbf{k}|$ in the neighborhood of $\mathbf{k}_m$, we may put $E(\mathbf{k}) = \hbar^2k^2/2m^\star$. Then (130) becomes

$$W(\mathbf{R}_{lm}) = \{|J(\mathbf{k}_m,\mathbf{k}_m)|^2m^\star V^2/(2\pi)^3R_{lm}^4\hbar^2N^2\}[2k_mR_{lm}\cos(2k_mR_{lm})$$
$$-\sin(2k_mR_{lm})](\mathbf{S}_l\cdot\mathbf{S}_m) \quad (132)$$

We have thus obtained the expression of indirect exchange coupling between two magnetic ions. The sign of (132) depends on $2k_mR_{lm}$, because it is determined by the function

$$(x\cos x - \sin x)/x^4$$

with $x = 2k_mR_{lm}$. The magnitude of the interaction drops off as R_{lm}^{-3}.

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FORBIDDEN TRANSITIONS IN ORGANIC AND INORGANIC SYSTEMS

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In 1933 Herzberg and Teller[8] demonstrated that certain electronic transitions which are forbidden in the fixed nuclei approximation may attain a non-zero transition probability through the interaction of electronic and nuclear motions. What they essentially did was to note that in every molecule there exist asymmetric nuclear displacements which yield a non-zero expectation value for the gradient of the nuclear–electronic coulombic energy terms. To illustrate their mode of thought we shall here give a pictorial outline of the calculation of such vibronic intensities in two systems of current interest: aromatic compounds and transition metal complexes. For the sake of clarity we shall limit our discussion to the exemplary molecular systems of benzene and potassium titanium hexafluoride (K_3TiF_6).

For electronic transitions the radiation probability or spectral strength is measured in terms of the so-called f-number or "oscillator strength." This number just expresses the probability of radiation emission or absorption in terms of the probability for an *equivalent* harmonic oscillator. That is, for an electronic transition $S \rightarrow N$, the f-number or oscillator strength is defined as

$$f(S \rightarrow N) = \frac{[dE(S \rightarrow N)/dt]_{\text{actual system}}}{[dE(S \rightarrow N)/dt]_{\text{equivalent harmonic oscillator}}} \qquad (1)$$

If f vanishes in the *fixed* nuclei approximation, the electronic jump is said to be "electronically forbidden"; if it vanishes also in the *moving* nuclei approximation, the spectral transition is said to be "vibronically (i.e., vibrationally–electronically) forbidden." Vibronically allowed emissions or absorptions are called Herzberg–Teller bands.

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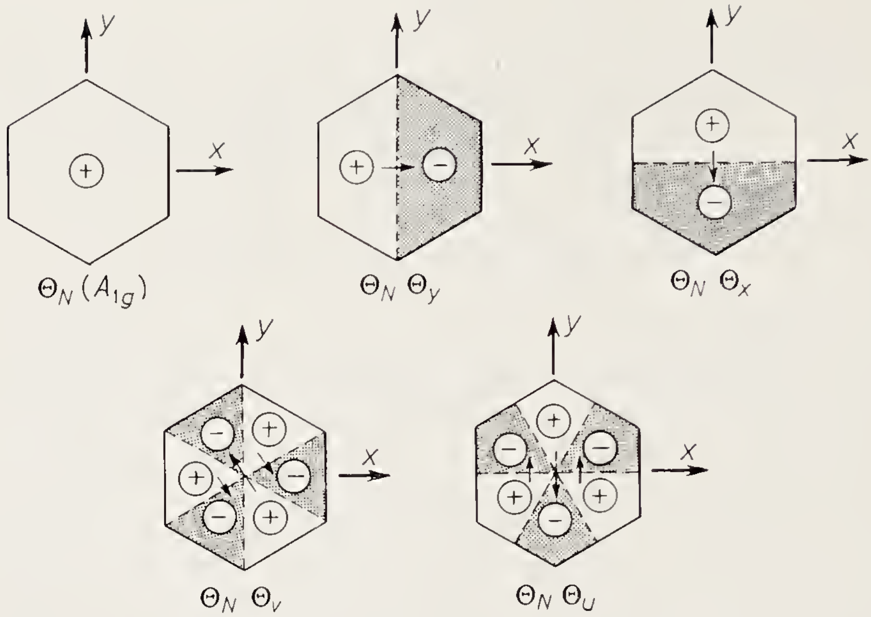


Fig. 1. The charge density function Θ_N which describes the $^1A_{1g}$ ground electronic state of benzene and its product densities with the excited $^1E_{1u}$ (Θ_x, Θ_y), $^1B_{1u}$ (Θ_u), and $^1B_{2u}$ (Θ_v) benzene states. It is seen that only the product density $\Theta_N\Theta_w$ $(w = x, y)$ may possess a net dipole moment for the benzene molecule and thus corresponds to an electronically allowed transition [since the "para"-dipole of the $\Theta_N\Theta_w$ $(w = u, v)$ product densities must have twice the strength of the "ortho"-dipole for the benzene geometry, it exhibits a cancellation of its internal dipole moment component parts].

The assessment of the oscillator strengths for electronically allowed bands is quite straightforward: all one need do is compute the transition dipole moment or transition probability, $e\langle N|\mathbf{r}|T\rangle$, which equals $e\int\Theta_N\mathbf{r}\Theta_T d\tau$ (see Fig. 1), and substitute in the formula

$$\begin{aligned} f(T \to N) &= \frac{8\pi^2 m\nu(T \to N)}{3e^2 h}\,|\langle N|\mathbf{r}|T\rangle|^2 \\ &= 1.085 \cdot 10^{11}\nu(T \to N;\ \mathrm{cm}^{-1})|\langle N|\mathbf{r}|T\rangle|^2 \end{aligned} \tag{2}$$

The evaluation of the comparable vibronically allowed spectral strengths is not so easy. For these systems two probabilities must be compounded: (1) the probability that our initial state, S say, has acquired some allowed character, T say, due to a vibronic disturbance ΔV_{ST}; and (2) the probability that it will radiate to the ground state, N say, while possessing this allowed character. (Similar arguments run through for the absorption process also. Here one wishes to compound the probability that the ground state N will absorb light while the excited state S has obtained some allowed character T through the action of the vibronic perturbation ΔV_{ST}.) In accordance with time-dependent perturbation theory, the first probability is given by[12a]

$$P_{S\to T}(t) = \frac{2|\Delta V_{ST}|^2 \sin^2 [\frac{1}{2}(\Delta E_{ST}/\hbar)]t}{\Delta E_{ST}^2} \tag{3}$$

The second probability is, of course, given in the units of oscillator strength by Eq. (2). *However, it is important to notice that the frequency of the radiated light is here* $\nu(S \to N)$ *although the relevant transition probability is* $e\langle N|\mathbf{r}|T\rangle$. This circumstance arises from the fact that the *energy* of our initial state, S, is not significantly altered by the perturbation ΔV, but the *charge density distribution* is. Indeed, it is just by virtue of the attainment of some allowed character, T, by means of Eq. (3), that our system may radiate at all. Hence, in the units of oscillator strength, our total radiation probability is

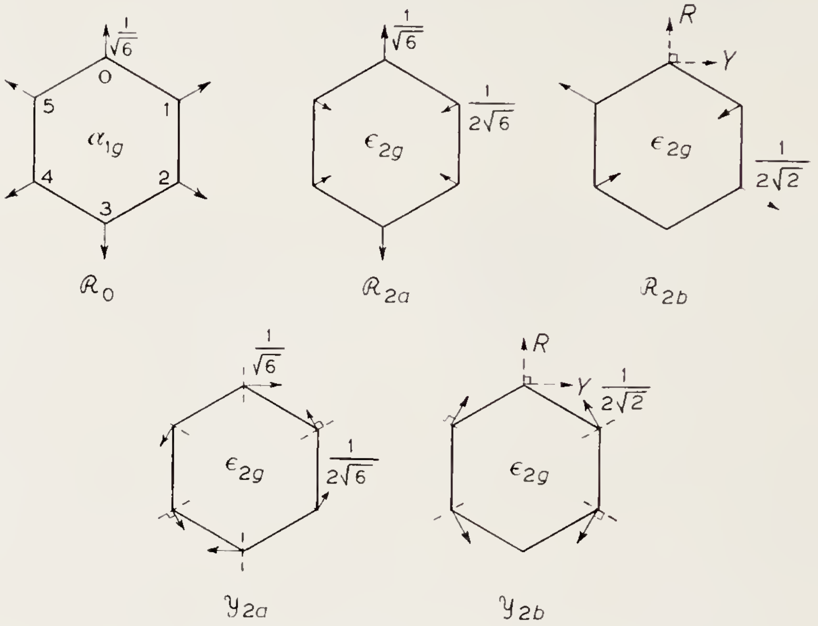
$$f_{S\to N}(t) = P_{S\to T}(t) \cdot 1.085 \cdot 10^{11}\nu(S \to N)|\langle N|\mathbf{r}|T\rangle|^2 \tag{4}$$

so that the time average probability is

$$f(S \to N) = \frac{|\Delta V_{ST}|^2}{\Delta E_{ST}^2} \cdot \frac{\nu(S \to N)}{\nu(T \to N)} \cdot f(T \to N) \tag{5}$$

We are now in a position to calculate radiation probabilities (i.e., intensities) for Herzberg–Teller type band systems.

To compute the intensity of the vibronic transition, $S \to N$, all we need do is evaluate the vibronic perturbation ΔV_{ST}: it is assumed that we have experimental or theoretical knowledge of the energies ΔE_{ST}, $h\nu(S \to N)$, and $h\nu(T \to N)$ and the electronically allowed oscillator strength $f(T \to N)$. [Experimentally, the latter may be obtained by the evaluation of the area under the absorption curve when its ordinate is the extinction coefficient, $\varepsilon(\nu)$, and its abscissa is the frequency of absorption, $\nu(\text{cm}^{-1})$, according to the formula $f = 4.33 \cdot 10^{-9}\int\varepsilon(\nu)d\nu$. Theoretically, it is obtained from Eq. (2).] Although this evaluation may be quite difficult if done nonempirically, the introduction of approximations permits a relatively simple specification of ΔV_{ST}. We shall illustrate such a semiempirical procedure for benzene and the titanium hexafluoride anion (TiF_6^{3-}) in a pictorial manner.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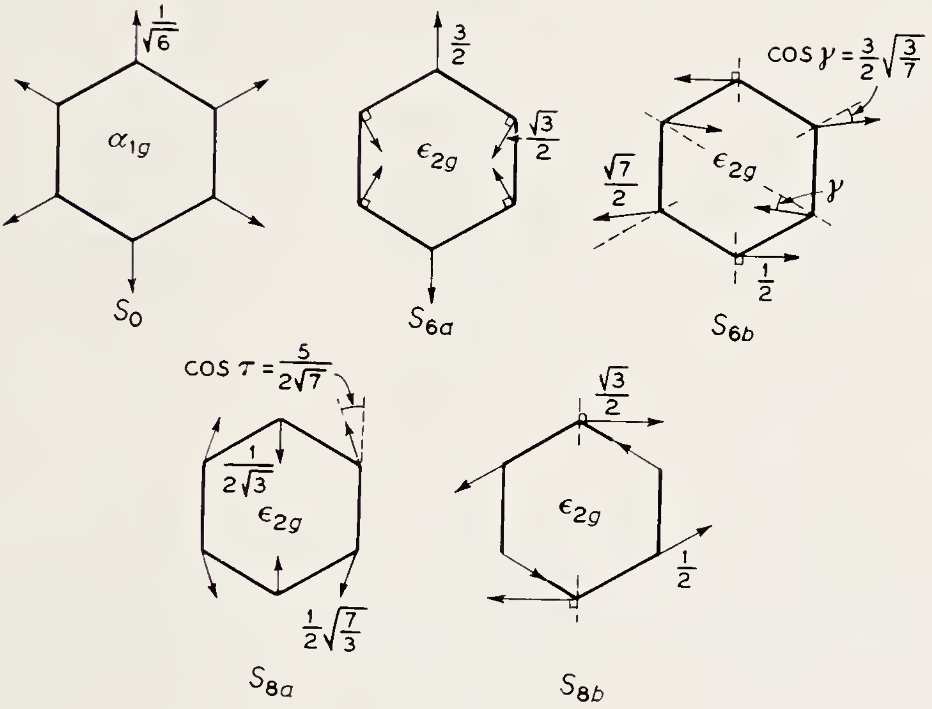
ϵ_{2g}
$\mathscr{Y}_{2b}$

Fig. 2. The α_{1g} and ε_{2g} carbon–carbon Cartesian symmetry displacements of benzene. The radial and tangential displacements R and Y, respectively, are positive at each atom in the direction indicated in $\mathscr{R}_{2b}$ and its clockwise rotated counterparts. The analogous *angle bending* and *bond stretching* displacements have been pictured in Fig. 3. A counterclockwise rotation of the molecule by 60° about the z-axis replaces $\mathscr{X}_{2a}$ by $-(1/2)\mathscr{X}_{2a} + (\sqrt{3}/2)\mathscr{X}_{2b}$, and $\mathscr{X}_{2b}$ by $-(\sqrt{3}/2)\mathscr{X}_{2a} - (1/2)\mathscr{X}_{2b}$ $(\mathscr{X} = \mathscr{R}, \mathscr{Y})$. [Such a physical rotation mathematically *replaces* atom r by $r - 1$.]

In Figs. 2 and 3 we have pictured the disturbing ε_{2g} nuclear displacements for the benzene electronic states ${}^1E_{1u}$, ${}^1B_{1u}$, and ${}^1B_{2u}$; and in Fig. 4 we depict the corresponding charge density functions for these same states. Now, recalling that the mathematical definition of a gradient is just the direction of change of a given property, we realize that Fig. 2 represents not only the direction and magnitude of nuclear displacements, but also the direction and magnitude of the nuclear gradients. In particular it correctly assesses the qualitative features of the gradient of the electron-nuclear potential V, that is, it assesses the form of the perturbation term ΔV of Eq. (5). Hence, as the coulombic perturbation energy ΔV_{ST} is defined as the sum (or integral) of the charge density distribution $\Theta_S\Theta_T$ times the gradient of the potential

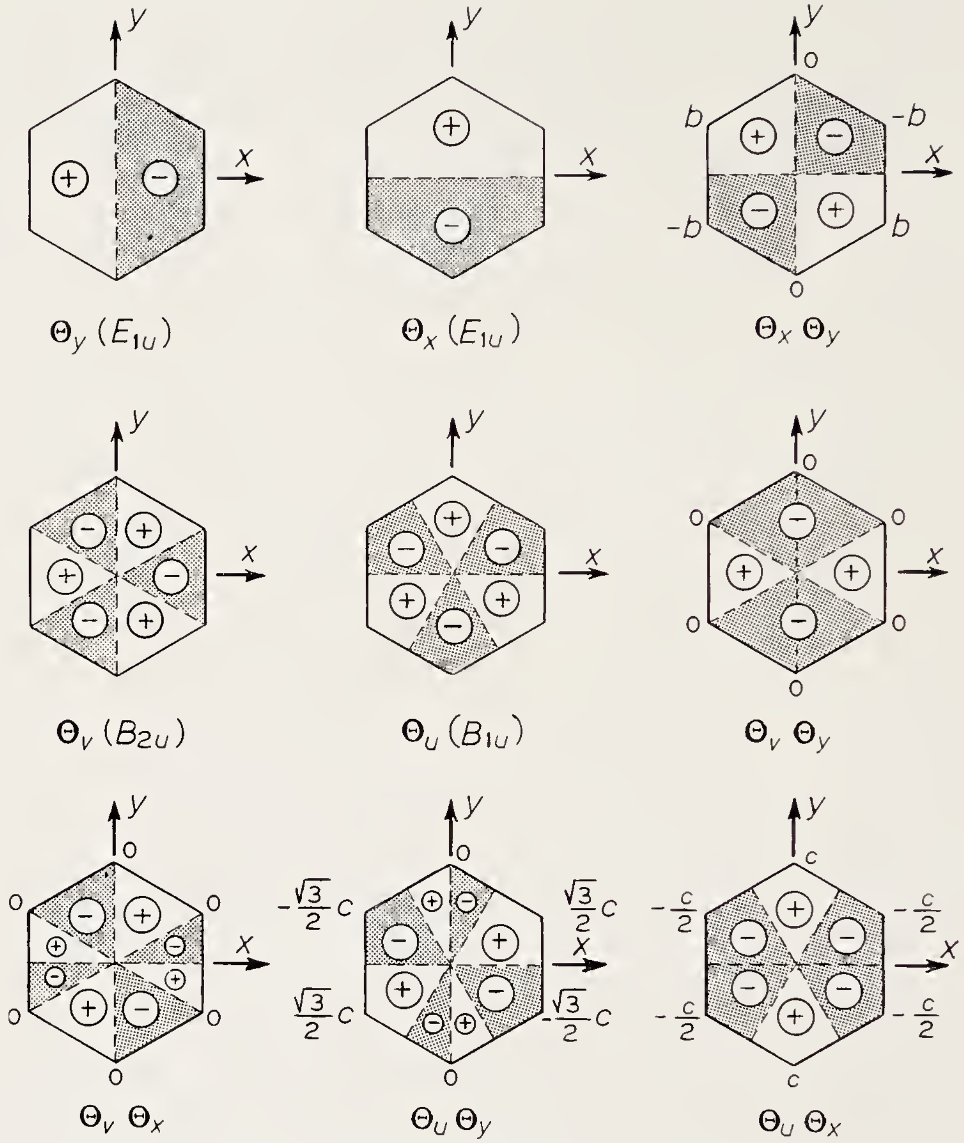
$$\Delta V_{ST} = \int \Theta_S \Theta_T \Delta V d\tau \tag{6}$$

we are now in a position to determine its magnitude.



$\frac{1}{\sqrt{6}}$
α_{1g}
S_0
$\frac{3}{2}$
$\frac{\sqrt{3}}{2}$
ϵ_{2g}
S_{6a}
$\cos\gamma = \frac{3}{2}\sqrt{\frac{3}{7}}$
$\frac{\sqrt{7}}{2}$
ϵ_{2g}
γ
$\frac{1}{2}$
S_{6b}
$\cos\tau = \frac{5}{2\sqrt{7}}$
$\frac{1}{2\sqrt{3}}$
ϵ_{2g}
$\frac{1}{2}\sqrt{\frac{7}{3}}$
S_{8a}
$\frac{\sqrt{3}}{2}$
ϵ_{2g}
$\frac{1}{2}$
S_{8b}

Fig. 3. The α_{1g} and ϵ_{2g} carbon–carbon internal symmetry displacements of benzene. A counterclockwise rotation of the molecule by 60° about the z-axis replaces S_{ka} by $-(1/2)S_{ka} - (\sqrt{3}/2)S_{kb}$, and S_{kb} by $(\sqrt{3}/2)S_{ka} - (1/2)S_{kb}$ $(k = 6, 8)$. (Please note the error in reference 12c: the counterclockwise rotation of the molecule there used was 60° *not* 120° as stated. Also, in Fig. 1 of 12c the signs in both Θ_x and $\Theta_x\Theta_y$ should be reversed.) The relationship connecting the Cartesian symmetry coordinates of Fig. 2 to the internal symmetry coordinates above is readily established by means of the vector addition of the appropriate displacement diagrams. This procedure yields $\mathscr{R}_0 = S_0$, $\mathscr{R}_{2\binom{a}{b}} = \pm(1/8)\sqrt{2/3} \times (3S_{6\binom{a}{b}} + \sqrt{3}S_{8\binom{a}{b}})$, and $\mathscr{Y}_{2\binom{a}{b}} = (1/8)\sqrt{2/3} \times (S_{6\binom{b}{a}} + 3\sqrt{3}S_{8\binom{b}{a}})$.


y
x
+
−
b
-b
-b
b
0
0
0
0
0
0
0
0
0
0
0
0
$-\frac{\sqrt{3}}{2}c$
$\frac{\sqrt{3}}{2}c$
$\frac{\sqrt{3}}{2}c$
$-\frac{\sqrt{3}}{2}c$
c
c
$-\frac{c}{2}$
$-\frac{c}{2}$
$-\frac{c}{2}$
$-\frac{c}{2}$

Θ_y (E_{1u}) Θ_x (E_{1u}) $\Theta_x\Theta_y$

Θ_v (B_{2u}) Θ_u (B_{1u}) $\Theta_v\Theta_y$

$\Theta_v\Theta_x$ $\Theta_u\Theta_y$ $\Theta_u\Theta_x$

Fig. 4. The charge density function Θ_w ($w = x, y, u, v$) of the $^1E_{1u}$ ($w = x, y$), $^1B_{1u}$ ($w = u$), and $^1B_{2u}$ ($w = v$) electronic states of benzene. Under a reflection in the nodal x,y plane (σ_h), all four of these functions remain unchanged. A counterclockwise rotation of the molecule by 60° about the z-axis replaces Θ_x by $(1/2)\Theta_x + (\sqrt{3}/2)\Theta_y$, Θ_y by $-(\sqrt{3}/2)\Theta_x + (1/2)\Theta_y$, and Θ_w by $-\Theta_w$ ($w = u, v$). The product densities $\Theta_s\Theta_w$ ($s = x, y$; $w = u, v$) are also pictured.

Let us first look at the term $\Delta V_{\left(\substack{x\\y}\right)v}$ which describes the mixing of the ${}^1B_{2u}$ and ${}^1E_{1u}$ states. We immediately see that as there is *zero* charge density at each atom in the charge density diagrams $\Theta_{\left(\substack{x\\y}\right)}\Theta_v$ of Fig. 4, the summation of Eq. (6) will be zero when we multiply the charge density at a given atom in Fig. 4 by the gradient distribution at each atom of Fig. 2. Thus, by Eq. (5), $f({}^1B_{2u} \rightarrow {}^1A_{1g})$ vanishes in this approximation. Experimentally, it is $\sim 10^{-3}$, and it can be shown that a more rigorous evaluation of Eq. (6) will indeed give this order of magnitude.[1,5,12a,15,16] What our model shows is that this quantity is very small, as is indeed observed.

We now examine the magnitude of the term $\Delta V_{\left(\substack{x\\y}\right)u}$ which portrays the scrambling of the ${}^1B_{1u}$ and ${}^1E_{1u}$ states. Multiplying the appropriate charge density and gradient patterns together we see that

$$\begin{aligned}
\Delta V_{yu} = {} & \frac{\sqrt{3}}{2}\, c \cdot (\text{constant})_1 \cdot \mathscr{R}_0 \left[\begin{aligned} & \frac{1}{\sqrt{6}}(0) + \frac{1}{\sqrt{6}}(-1) + \frac{1}{\sqrt{6}}(1) \\ & + \frac{1}{\sqrt{6}}(0) + \frac{1}{\sqrt{6}}(-1) + \frac{1}{\sqrt{6}}(1) \end{aligned} \right] \\
& + \frac{\sqrt{3}}{2}\, c \cdot (\text{constant})_2 \mathscr{R}_{2a}[0] + \frac{\sqrt{3}}{2}\, c \cdot (\text{constant})_3 \mathscr{R}_{2b}\left[4 \cdot \frac{1}{2\sqrt{2}}\right] \\
& + \frac{\sqrt{3}}{2}\, c \cdot (\text{constant})_4 \mathscr{Y}_{2b}[0] + \frac{\sqrt{3}}{2}\, c \cdot (\text{constant})_5 \mathscr{Y}_{2a}\left[4 \cdot \frac{1}{2\sqrt{6}}\right] \\
\Delta V_{yu} = {} & \sqrt{3/2}(ck_3\mathscr{R}_{2b}) + \sqrt{1/2}(ck_5\mathscr{Y}_{2a}) \qquad (7)
\end{aligned}$$

where the "constants" (later symbolized by k) assess the magnitude of the derivative of the potential at each atom.* Similarly,†

$$\Delta V_{xu} = \sqrt{3/2}(ck_6\mathscr{R}_{2a}) + \sqrt{1/2}(ck_7\mathscr{Y}_{2b}) \qquad (8)$$

Explicit evaluation of the constants c and k_j, ($j = 3, 5, 6, 7$), by taking the gradient of the Lennard-Jones approximation for the resonance integral, $\beta_{rs} = \int \varphi_r \mathscr{H} \varphi_s d\tau$, where $\varphi_{r,s}$ are carbon $2p_z$ orbitals located at atoms r and s, $\mathscr{H}$ is the appropriate one-electron Hamiltonian, and where the Lennard-Jones expression is

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* See note on page 259.

† The constants k_j, ($j = 3, 5, 6, 7$), of Eqs. (7) and (8) may be simply related by recognizing that an integral (*a number*) must be an invariant under all coordinate transformations. See Appendix 1.

$$\beta_{rs} = \frac{\kappa}{4}[(x_{r,s} - d)^2 - (x^0 - d)^2] - \frac{\sigma}{4}[(x_{r,s} - s)^2 - (x^0 - s)^2] \quad (9)$$

$\kappa =$ double bond force constant in ethylene
$\sigma =$ single bond force constant in ethane
$d =$ double bond length in ethylene
$s =$ single bond length in ethane (10)

leads to a value of $f(^1B_{1u} \rightarrow {}^1A_{1g})$ of $\sim 10^{-1}$, which is in excellent agreement with experiment. The inclusion of non-zero overlap between the $2p_z$ orbitals also allows one to predict that

$$f(^1B_{2u} \rightarrow {}^1A_{1g}) : f(^1B_{1u} \rightarrow {}^1A_{1g}) \sim 10^{-2}$$

which is also observed experimentally.[12a]

It might be profitably noted here that the charge density pattern $\Theta_x \cdot \Theta_y$ shows that the two charge distributions Θ_x and Θ_y of the $^{1,3}E_{1u}$ electronic state may interact. Such interactions of the components of a degenerate electronic state are called Jahn–Teller interactions. However, closer inspection of the wave functions of the $^{1,3}E_{1u}$ state shows that only two-electron coulombic terms such as $\langle e^2/r_{12} \rangle$ yield a non-zero Jahn–Teller energy for the $^{1,3}E_{1u}$ state of benzene. This is not the case for

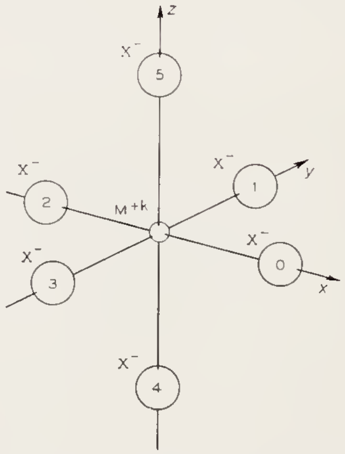

Fig. 5. The geometrical disposition of a hexacoordinated inorganic complex.

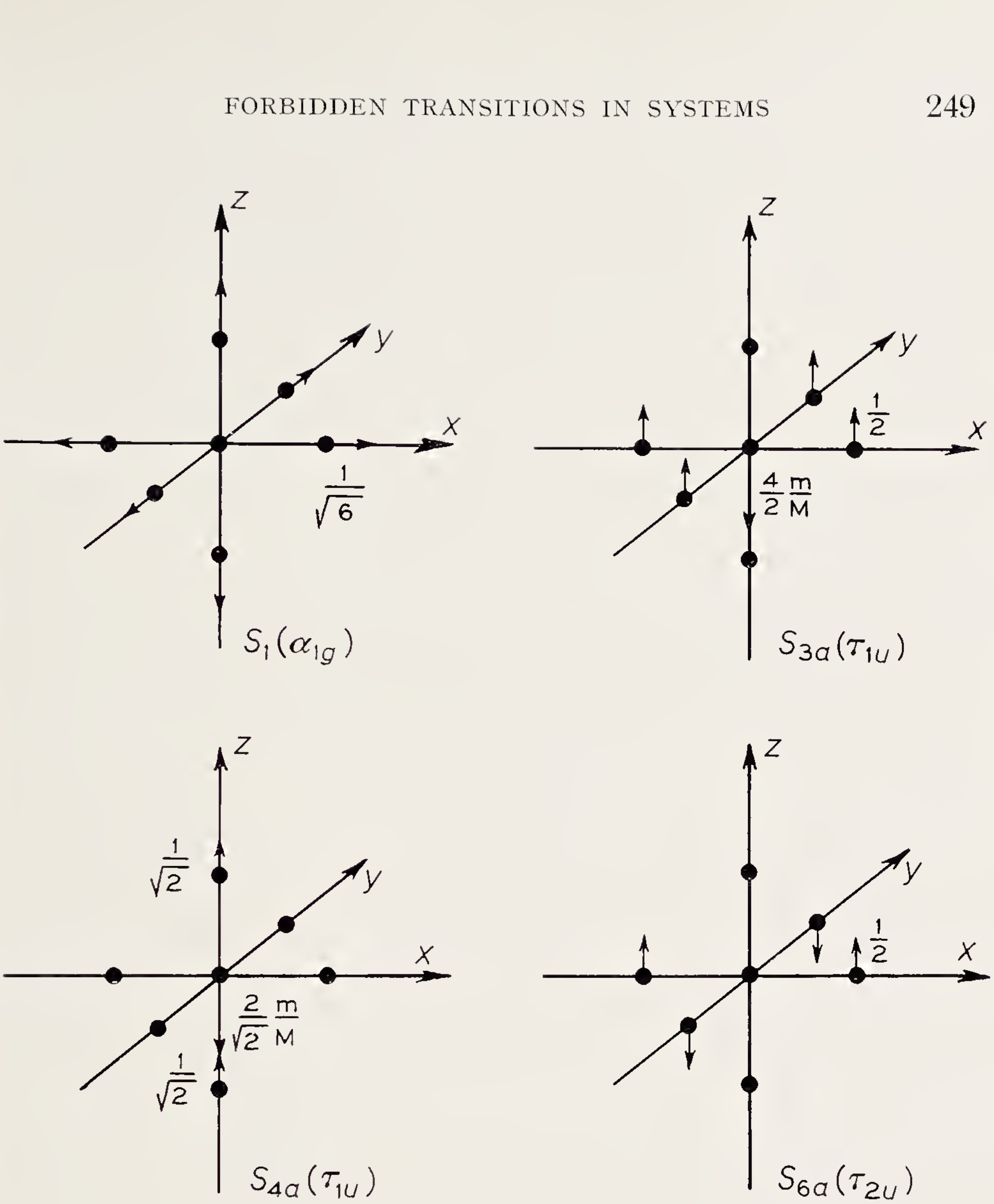
z
y
x
$\frac{1}{\sqrt{6}}$
$S_1(\alpha_{1g})$
z
y
x
$\frac{1}{2}$
$\frac{4}{2}\frac{m}{M}$
$S_{3a}(\tau_{1u})$
z
$\frac{1}{\sqrt{2}}$
y
x
$\frac{2}{\sqrt{2}}\frac{m}{M}$
$\frac{1}{\sqrt{2}}$
$S_{4a}(\tau_{1u})$
z
y
$\frac{1}{2}$
x
$S_{6a}(\tau_{2u})$

Fig. 6. The totally symmetrical α_{1g} and the odd τ_{1u} and τ_{2u} nuclear displacements of a hexacoordinated inorganic complex (e.g., TiF_6^{3-}). Only one component of the triply degenerate τ displacements is shown. The others are simply obtained by a counterclockwise rotation of the coordinates by 120° about the (111) direction. As such a rotation *replaces* x by z, y by x, z by y, atom 0 by 5, 1 by 0, 2 by 4, 3 by 2, 4 by 3, and 5 by 1. The displacement arrows are then parallel to the y-axis for "b" displacements and to the x-axis for "c" displacements (see also reference 13b).

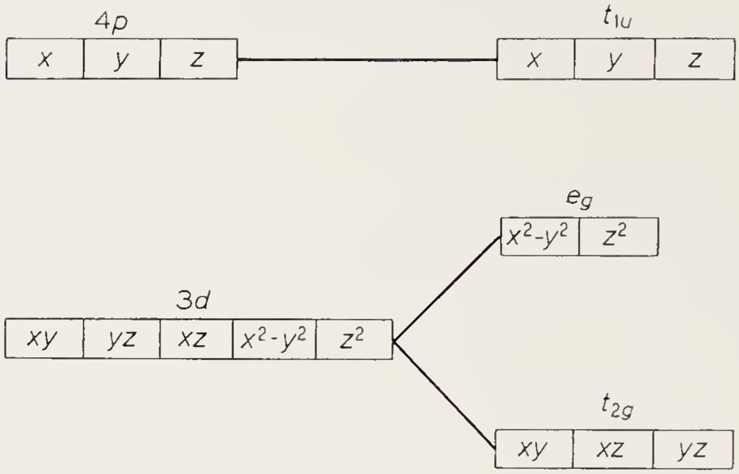
4p
x
y
z
t_{1u}
x
y
z
e_g
x^2-y^2
z^2
3d
xy
yz
xz
x^2-y^2
z^2
t_{2g}
xy
xz
yz

Fig. 7. The energy levels of a hexacoordinated "ionic" complex.

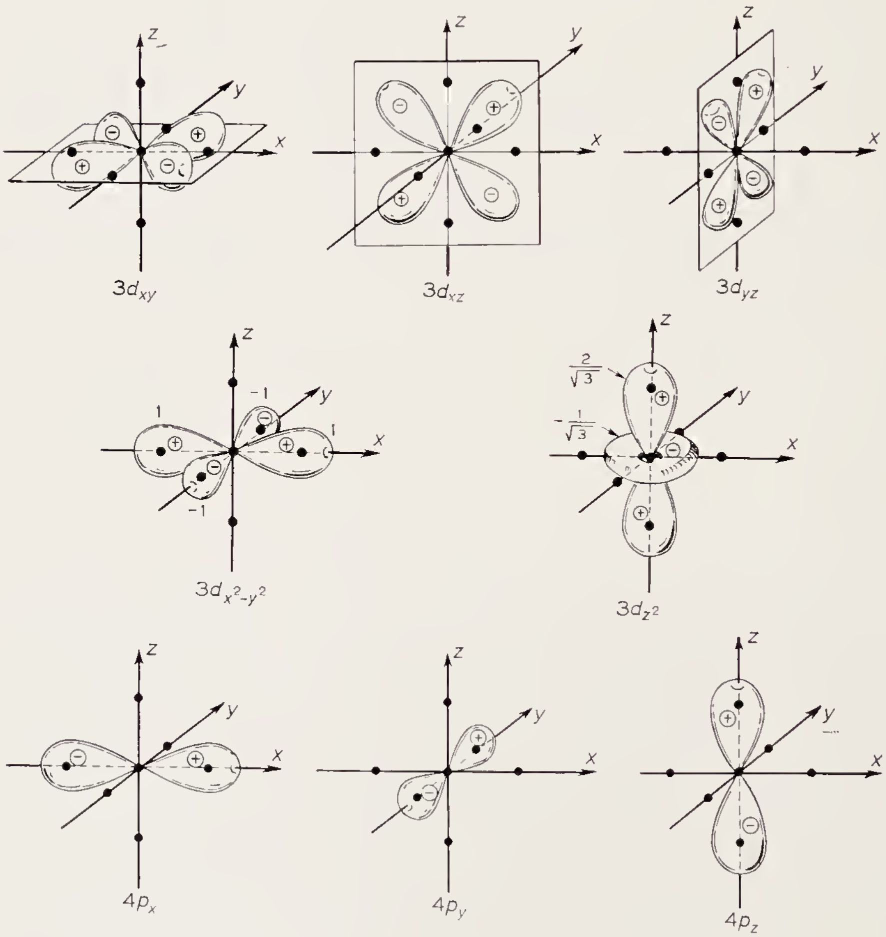
$3d_{xy}$
$3d_{xz}$
$3d_{yz}$
$3d_{x^2-y^2}$
1
-1
1
-1
$3d_{z^2}$
$\frac{2}{\sqrt{3}}$
$-\frac{1}{\sqrt{3}}$
$4p_x$
$4p_y$
$4p_z$
x
y
z

Fig. 8. The $3d$ and $4p$ orbitals in an octahedral field.

the $^2E_{1g}$ ground state of the uni-positive and uni-negative ions of benzene which show large Jahn–Teller deformations.[8,12a,14,20] A pictorial outline of this latter Jahn–Teller problem is given in reference 12c. In addition, it may be shown that pseudo Jahn–Teller forces strongly mix the $^{1,3}B_{1u}$ and $^{1,3}E_{1u}$ states, so that the geometry of the former state is drastically altered.[12a]

In Fig. 5 we show the geometry assumed by a typical octahedral inorganic complex, and in Figs. 6, 7, and 8 we depict the behavior of the nuclear motions, electronic energies, and charge amplitude functions of an exemplary such system, TiF_6^{3-}. As Ti^{3+} has the electronic structure $[A]3d^1$, its ground electronic state is $^2T_{2g}$ by Fig. 7, and its first excited state is ^2E_g. By the parity rule $g \nleftrightarrow g$, we see that the emission $^2E_g \rightarrow {}^2T_{2g}$ is electronically forbidden. However, as with benzene, asymmetric vibrations may mix in some of the allowed $^2T_{1u}(4p)$ state* and make the transition vibronically allowed (see Fig. 9). Evaluation of the vibronic perturbation ΔV_{ST} of Eq. (6) cannot be performed in the simple way it was done for benzene. However, an investigation of the symmetry

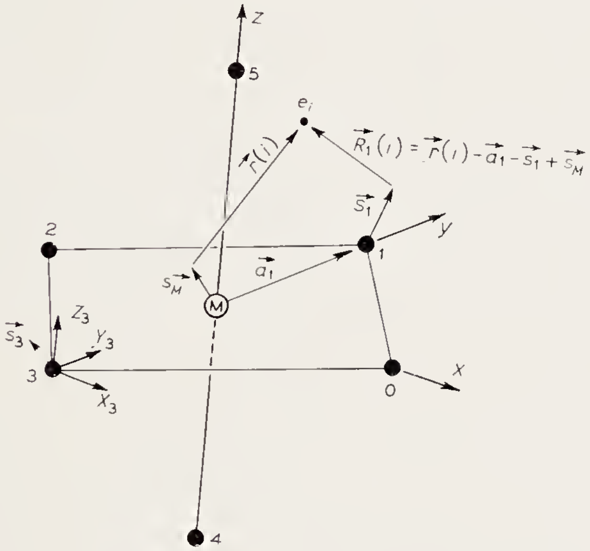

Fig. 9. A general displacement vector of an octahedral complex. Such vectors may be uniquely expressed as a linear combination of the symmetry displacements (e.g., see Fig. 6), which in turn may be expressed as linear combinations of the normal coordinates.

---

* The $^2T_{1u}$ state is here designated by "4p" for illustrative clarity only. In general, it is a state described by both the metallic 4p atomic functions and the ligand t_{1u} π- and σ-bonding molecular orbitals.[13a]

properties of the integrals $\Delta V_{i,j} = \int 4p_i \Delta V(S_k) 3d_j d\tau$ ($i = x,y,z$: $j = xy,xz,yz,x^2 - y^2,z^2$: $k = 1;3a,b,c;4a,b,c;6a,b,c$), under reflections in the six $y = 0$, $x = 0$, $z = 0$, $x = z$, $y = z$, and $x = y$ planes allows their general form to be determined. For example, as the $4p_i$ functions transform as (x,y,z), and the $3d_{xy}$ function as xy, and the *gradients* with respect to S_{ka}, S_{kb}, S_{kc} ($k = 3, 4, 6$), transform as z, y, and x, respectively (see Fig. 5), we see that the electronic integral $\Delta V_{xy,z}$ transforms as $xyz \cdot \text{gradient}\ (S_{ka,b,c})$, which is therefore always *odd* under some reflection plane. This implies that the integral, which is a number and hence cannot be affected by such reflections, must vanish. The end result of such continued argumentation is listed below.

$$\begin{aligned}
\Delta V_{xy,x} &= \gamma^{xy}_{x,3b} S_{3b} + \gamma^{xy}_{x,4b} S_{4b} + \gamma^{xy}_{x,6b} S_{6b} \\
\Delta V_{xy,y} &= \gamma^{xy}_{y,3c} S_{3c} + \gamma^{xy}_{y,4c} S_{4c} + \gamma^{xy}_{y,6c} S_{6c} \\
\Delta V_{xy,z} &= 0, \text{ etc.}
\end{aligned} \tag{11}$$

$$\begin{aligned}
\Delta V_{x^2-y^2,x} &= \gamma^{x^2-y^2}_{x,3c} S_{3c} + \gamma^{x^2-y^2}_{x,4c} S_{4c} + \gamma^{x^2-y^2}_{x,6c} S_{6c} \\
\Delta V_{x^2-y^2,y} &= \gamma^{x^2-y^2}_{y,3b} S_{3b} + \gamma^{x^2-y^2}_{y,4b} S_{4b} + \gamma^{x^2-y^2}_{y,6b} S_{6b} \\
\Delta V_{x^2-y^2,z} &= \gamma^{x^2-y^2}_{z,6a} S_{6a}, \text{ etc.}
\end{aligned} \tag{12}$$

The remaining vibronic perturbation terms are readily obtained from Eqs. (11) and (12) upon application of a counterclockwise rotation of 120° about the (111) direction. Such a rotation *replaces* x by z, y by x, z by y, and correspondingly, a-type displacements by b-type, b-type by c-type, and c-type by a-type; thus, it replaces $d_{x^2-y^2}$ by

$$(\sqrt{3}/2)d_{z^2} - \tfrac{1}{2}d_{x^2-y^2}$$

and d_{z^2} by

$$-\tfrac{1}{2}d_{z^2} - (\sqrt{3}/2)d_{x^2-y^2}$$

These replacement relations then transform one set of ΔV_{ST} elements into the others (see Appendix 2).

As the various energy terms in Eq. (5) have not yet been experimentally determined for K_3TiF_6, we shall instead compute the intensities of the electronically similar $Ti(H_2O)_6^{3+}$ ion. The numerical evaluation of the interaction terms ΔV_{ST} for this latter system and the substitution into Eq. (5) yields an oscillator strength of $1.4 \cdot 10^{-4}$, which is in good agreement with the experimental value of $1.1 \cdot 10^{-4}$.[6,13a]

Needless to say, the vibronic theory outlined here is quite general and has been applied by myself and others to a large number of molecular systems.[1,4–7,9–13,15–19,21–23] So far the theoretical predictions have been most gratifying. However, it must be said that more thoroughgoing calculations show the need for extreme caution in utilizing these more simple models.[12d] (See Appendices 2 and 3.)

In closing I should like to express my deep indebtedness to the late Professor William E. Moffitt who initiated and encouraged my interest in vibronic phenomena, both as a graduate student and as a post-graduate scientist. My scientific outlook and approach to such problems stem quite directly from his inspirational guidance. It is with great sadness that I now look back at the untimely death of this fine human being.

I should also like very much to thank my good friend Carl J. Ballhausen for introducing me to crystal field theory (unpublished lectures, Department of Chemistry, Harvard University, Fall 1955), and for our years of happy collaborative effort together, which collaboration resulted in the rigorous ligand field solution of the inorganic intensity problem.

Finally, I should like to thank my many friends and colleagues who freely discussed their closely related researches with me, and who, in many instances, were able to provide me with preprints of their work.

APPENDIX 1

To relate the constants k_j, $(j = 3, 5, 6, 7)$, of Eqs. (7) and (8) one to another, one need only invoke the invariance of an integral to its coordinate basis. For example, according to the caption of Fig. 4, the left-hand side of Eq. (7),

$$\Delta V_{yu} = \int \Theta_y \Theta_u \Delta V \tag{A1-1}$$

may be rewritten, upon a counterclockwise rotation of the benzene molecule about its z-axis, as

$$\begin{aligned}(\Delta V_{yu})_{\text{rotated}} &= \left[\int \Theta_y \Theta_u \Delta V\right]_{\text{rotated}} \\ &= \frac{\sqrt{3}}{2}\,\Delta V_{xu} - \frac{1}{2}\,\Delta V_{yu}\end{aligned} \tag{A1-2}$$

since energy terms such as ΔV, being *physical* quantities, are invariant under all molecular symmetry operations. Likewise, according to the caption of Fig. 2, the left-hand side of Eq. (7) may be rewritten as

$$(\Delta V_{yu})_{\text{rotated}} = \sqrt{\frac{3}{2}}\, ck_3 \left[\frac{-\sqrt{3}}{2}\mathscr{R}_{2a} - \frac{1}{2}\mathscr{R}_{2b}\right] + \sqrt{\frac{1}{2}}\, ck_5 \left[\frac{-1}{2}\mathscr{Y}_{2a} + \frac{\sqrt{3}}{2}\mathscr{Y}_{2b}\right] \quad \text{(A1-3)}$$

But, since the substitution of Eqs. (7) and (8) into (A1-2) yields

$$(\Delta V_{yu})_{\text{rotated}} = \frac{\sqrt{3}}{2}\left[\sqrt{\frac{3}{2}}\, ck_6\mathscr{R}_{2a} + \sqrt{\frac{1}{2}}\, ck_7\mathscr{Y}_{2b}\right] - \frac{1}{2}\left[\sqrt{\frac{3}{2}}\, ck_3\mathscr{R}_{2b} + \sqrt{\frac{1}{2}}\, ck_5\mathscr{Y}_{2a}\right] \quad \text{(A1-4)}$$

a direct comparison of the identities (A1-3 and 4) gives the desired relationship between the constants k_j: $k_3 = -k_6$ and $k_5 = k_7$.

APPENDIX 2

The algebraic forms of the inorganic vibronic coupling constants $\gamma^{xy}_{x,3b}$, etc., computed on the basis of a point charge model,[13a] have not been previously published. For the sake of completeness, we list these below:

$$\gamma^{xy}_{x,3b} = \gamma^{xy}_{y,3c} = -\frac{1}{\sqrt{5}}\frac{qe^2}{a}\left[\frac{9}{7}G_3 + 2G_1\right]$$

$$\gamma^{xy}_{x,4b} = \gamma^{xy}_{y,4c} = -\sqrt{\frac{2}{5}}\, qe^2\left[-\frac{3}{7}B_3 + B_1\right]$$

$$\gamma^{xy}_{x,6b} = \gamma^{xy}_{y,6c} = -\frac{3\sqrt{5}}{7}\frac{qe^2}{a}G_3 \quad \text{(A2-1)}$$

$$\gamma^{x^2-y^2}_{x,3c} = -\gamma^{x^2-y^2}_{y,3b} = -\sqrt{\frac{1}{5}}\frac{qe^2}{a}\left(-\frac{27}{14}G_3 + 2G_1\right)$$

$$\gamma^{x^2-y^2}_{x,4c} = -\gamma^{x^2-y^2}_{y,4b} = -\sqrt{\frac{2}{5}}\, qe^2\left[\frac{9}{14}B_3 + B_1\right]$$

$$\gamma^{x^2-y^2}_{x,6c} = -\gamma^{x^2-y^2}_{y,6b} = +\frac{3\sqrt{5}}{14}\frac{qe^2}{a}G_3 \quad \text{(A2-2)}$$

where

$$G_l = \int_0^\infty R_{3d}(r) \frac{1}{r_>} \left(\frac{r_<}{r_>}\right)^l R_{4p}(r) r^2 dr, \quad B_l = \frac{d}{da} G_l \qquad \text{(A2-3)}$$

a is the metal–ligand bond distance, and qe is the charge on a given ligand. These integrals have recently been tabulated.[3]

As mentioned in the text proper, the remaining vibronic constants are readily obtained by use of the three-fold symmetry about the (111) direction [since the γ's are *numbers* (definite integrals) a rotation about this three-fold axis *cannot* change their value; hence, if such a rotation relates one γ to another, they must perforce be equal]. For example, if $\mathscr{C}_3$ represents this counterclockwise rotation operation, then $\gamma^{xz}_{z,3c} = \mathscr{C}_3 \gamma^{xy}_{x,3b} \equiv \gamma^{xy}_{x,3b}$. Also, $\gamma^{x^2-y^2}_{y,3b} \equiv \mathscr{C}_3 \gamma^{x^2-y^2}_{y,3b} = (\sqrt{3}/2)\gamma^{z^2}_{x,3c} - (1/2)\gamma^{x^2-y^2}_{x,3c}$, or since $\gamma^{x^2-y^2}_{x,3c} = -\gamma^{x^2-y^2}_{y,3b}$, we must have $\gamma^{z^2}_{x,3c} = -(1/\sqrt{3})\gamma^{x^2-y^2}_{x,3c}$, etc. The relationship between $\gamma^{xy}_{x,kb}$ and $\gamma^{xy}_{y,kc}$, and $\gamma^{x^2-y^2}_{x,kc}$ and $\gamma^{x^2-y^2}_{y,kb}$ $(k = 3, 4, 6)$, is readily derived upon application of a reflection in the $x = y$ plane (such a reflection *replaces* x by y, y by x, z by z, and correspondingly, a-type displacements by a-type, b-type by c-type, and c-type by b-type). Other useful relationships may be similarly derived from other symmetry operations (i.e., coordinate transformations). In utilizing the $\mathscr{C}_3$ operation on the symmetry displacements $S_{ka,b,c}$, it is important to note that, although $\mathscr{C}_3 k \begin{pmatrix} a \\ b \\ c \end{pmatrix} = k \begin{pmatrix} b \\ c \\ a \end{pmatrix}$, $(k = 3, 4)$, as stated in the main text, the corresponding relations for the $6a,b,c$ displacements are

$$\mathscr{C}_3 6 \begin{pmatrix} a \\ b \\ c \end{pmatrix} = 6 \begin{pmatrix} -b \\ -c \\ a \end{pmatrix}.$$

The final intensities for such inorganic systems are then straightforwardly computed by means of Eq. (5), once the symmetry coordinates, S_{kP}, have been replaced by the proper normal modes, Q_{jP}, by means of the equation [see reference 13b]*

$$S_{kP} = \sum L_{kj} Q_{jP} \qquad (k,j = 3, 4, 6) \qquad (P = a, b, c) \qquad \text{(A2-4)}$$

* The L matrix given in reference 13b was determined using an orthonormal set of *internal* symmetry coordinates, rather than the cartesian coordinates listed. This use gives rise to the $\sqrt{2}$ factor in Eq. (15) of reference 13b.

A set of vectorial identities which are useful in deriving Eqs. (A2-1 and 2) are listed below. The symbolism employed is that defined in Fig. 9.[13]

$$\begin{aligned}
\hat{a}_j \cdot (\mathbf{s}_j - \mathbf{s}_M) &= \eta_j \\
\hat{\theta}_j \cdot (\mathbf{s}_j - \mathbf{s}_M) &= -(Z_j - Z_M), \qquad (j = 0, 1, 2, 3) \\
\cos \varphi_j \hat{\theta}_j \cdot (\mathbf{s}_j - \mathbf{s}_M) &= (-1)^{j-1}(X_j - X_M), \qquad (j = 4, 5) \\
\sin \varphi_j \hat{\theta}_j \cdot (\mathbf{s}_j - \mathbf{s}_M) &= (-1)^{j-1}(Y_j - Y_M), \qquad (j = 4, 5) \\
\hat{\varphi}_{\binom{0}{2}} \cdot (\mathbf{s}_{\binom{0}{2}} - \mathbf{s}_M) &= \pm(Y_{\binom{0}{2}} - Y_M) \\
\hat{\varphi}_{\binom{1}{3}} \cdot (\mathbf{s}_{\binom{1}{3}} - \mathbf{s}_M) &= \mp(X_{\binom{1}{3}} - X_M) \\
\hat{\varphi}_j \cdot (\mathbf{s}_j - \mathbf{s}_M) &= 0, \qquad (j = 4, 5)
\end{aligned} \tag{A2-5}$$

where η_j is the bond stretching coordinate corresponding to the ligand j.

It should be mentioned here that attempts to use the matrix sum rule to evaluate vibronic intensities introduces unnecessary errors. *The sum rule can only be applied when one is dealing with a complete set of wave functions.* The use of approximate wave functions, incomplete sets, etc., invalidates the matrix closure rules. This statement applies to *both* the electronic and vibrational problems separately and jointly (see, e.g., reference 1).

For future reference, we list below the intensity distribution, at absolute zero, amongst the various vibrational levels of the complexes of Ti^{3+}, V^{3+}, Ni^{2+}, and Cu^{2+}. In the ionic approximation these ratios are independent of the ligand field and the $3d$–$4p$ energy separation. They depend only upon the metal–ligand bond distance and the $3d$ and $4p$ effective nuclear charges.[4,13a]

TABLE I. Intensity Ratios

M	Transition	$\nu_4(\tau_{1u}):\nu_3(\tau_{1u})$	$\nu_4(\tau_{1u}):\nu_6(\tau_{2u})$
Ti^{3+}	$^2T_{2g} \rightarrow {}^2E_g$	1.3:1	1.4:1
V^{3+}	$^3T_{1g} \rightarrow {}^3T_{2g}$	5.6:1	31:1
	$^3T_{1g} \rightarrow {}^3T_{1g}$	2.4:1	24:1
	$^3T_{1g} \rightarrow {}^3A_{2g}$	1:1.5	364:1
Ni^{2+}	$^3A_{2g} \rightarrow {}^3T_{2g}$	3.1:1	2.9:1
	$^3A_{2g} \rightarrow {}^3T_{1g}$ or $^3T_{1g}^*$	1:6.5	1.7:1
Cu^{2+}	$^2E_g \rightarrow {}^2T_{2g}$	2.0:1	16:1

These values must be used only with great caution, as even the most thoroughgoing of calculations has not yet succeeded in predicting *individual* vibrational sublevel intensities correctly.[4,12c,d]*

APPENDIX 3

The recent recurrence of interest in vibronic calculations on the benzene molecule[1] prompts the inclusion in this appendix of the vibronic coupling constants which I computed some years back.[12d] These constants, when substituted into Eq. (15) of reference 12a, yield the requisite vibrational sublevel intensities. The notation is that which I have used in my previous publications on this topic. In the following tables, the references to "Eqs. (2), (6), (7), and (10)" are to the appropriate equations in reference 12d. As mentioned in Appendix 2, great caution must be used in making predictions of sublevel intensities from such tables, though. The violence of the approximations utilized in going from one column to another in Tables II and III is reflected in

TABLE II. Nonempirical Calculations[a]

Vibronic constants (units of $\frac{Z^2e^2}{a_0^2}\cdot 10^{-3}$)	Equation (2)	Equation (6), expt'l. ΔE's	Equation (6), theor. ΔE's	Equation (7)
D_{M6}	$+0.04551$	-2.1284	-2.1012	-2.1602
D_{M7}	-0.1717	-0.2251	-0.2019	-0.2521
D_{M8}	-0.8836	$+1.8108$	$+1.8848$	$+1.7245$
D_{M9}	-0.2388	-0.007034	$+0.02052$	-0.03918
$D_{\Lambda 6}$	$+1.4606$	$+0.8377$	$+0.7497$	$+0.8791$
$D_{\Lambda 7}$	-1.0389	-0.4494	-0.4001	-0.4725
$D_{\Lambda 8}$	-6.9531	-3.2868	-2.9316	-3.4540
$D_{\Lambda 9}$	-1.6100	-0.7251	-0.6462	-0.7623

[a] Equation numbers are from reference 12d.

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* In the computation of the oscillator strengths in reference 13a, a common vibronic perturbation denominator, $E_p - E_d$, was utilized for both the t_{2g} and e_g orbitals, for reasons of simplicity. Also, the Rydberg constant R entered the final formulas as an abbreviation for the quantity $(e^2/2a_0)$.

TABLE III. Semiempirical Calculations[a]

Vibronic constants (units of $\frac{Z^2e^2}{a_0^2}\cdot 10^{-3}$)	Equations (10) and (7), $Z_a = 1$	Equations (10) and (7), with Craig's screening, $Z_a = \sqrt{2}$	Equations (10) and (7), zero overlap, etc., $Z_a = Z'$	Lennard–Jones approximation[12a,d]
D_{M6}	$+1.66$	$-0.592\sqrt{2}$	$+1.78Z'$	0
D_{M7}	$+0.206$	$+0.0169\sqrt{2}$	$+0.218Z'$	0
D_{M8}	-1.26	$+0.884\sqrt{2}$	$-1.37Z'$	0
D_{M9}	$+0.0474$	$+0.106\sqrt{2}$	$+0.0456Z'$	0
$D_{\Lambda 6}$	-0.375	$-0.935\sqrt{2}$	$-0.757Z'$	$+0.936$
$D_{\Lambda 7}$	$+0.127$	$+0.0799\sqrt{2}$	$+0.0728Z'$	-0.598
$D_{\Lambda 8}$	$+1.12$	$+1.65\sqrt{2}$	$+1.38Z'$	-4.13
$D_{\Lambda 9}$	$+0.224$	$+0.239\sqrt{2}$	$+0.204Z'$	-0.940

[a] Equation numbers are from reference 12d.

the sign changes of the vibronic coupling parameters there tabulated. Please note that in computing intensities from these tables (as was done in reference 12d), care must be taken to properly normalize the perturbed wave functions, for in some instances the perturbations produce a nonnegligible change in these quantities.

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* *Note added in proof* (see p. 247). A bit of subterfuge has been employed here as the *simple* classical charge density times a potential energy gradient pattern picture breaks down for tangential gradients (due to the equivalence of positive and negative tangential coulombic gradient interactions with point charges—compare pp. 251ff and references 12b and 12c). To obtain

equations (7) and (8) rigorously, one notes that equation (6) vanishes identically whenever the charge density and potential gradient patterns are of opposite parity under some coordinate transformation. Hence, as the charge density pattern $\Theta_y \cdot \Theta_u$ is of odd parity (i.e., it changes sign) when reflected in the planes $x = 0$ and $y = 0$, and the charge density pattern $\Theta_x \cdot \Theta_u$ is of even parity (i.e., it does not change sign) under these same reflections (see Fig. 4), these charge densities can interact only with potential gradients which are respectively odd and even. Since it is the potential energy gradient patterns with respect to $\mathscr{R}_{2b}$ and $\mathscr{Y}_{2a}$ which are odd, and those with respect to $\mathscr{R}_{2a}$ and $\mathscr{Y}_{2b}$ which are even under reflections in the $x = 0$ and $y = 0$ planes (see Fig. 2), we may conclude, without approximation, that the vibronic interaction energy ΔV_{yu} can only depend upon $\mathscr{R}_{2b}$ and $\mathscr{Y}_{2a}$ linearly, and the vibronic interaction energy ΔV_{xu} only upon $\mathscr{R}_{2a}$ and $\mathscr{Y}_{2b}$ linearly, as stated in the text [equations (7) and (8)]. We shall discuss this technique of determining the *exact* functional form of vibronic integrals through symmetry arguments further on pp. 251ff (in this regard read also references 12b and 12c), when we consider the exemplary inorganic compound potassium titanium hexafluoride.

THE FORMAL STATISTICAL THEORY OF TRANSPORT PROCESSES

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I. INTRODUCTION

The description of a system in thermodynamic equilibrium is, in principle, quite simple. For fixed values of the volume, energy, particle number, and of any other controllable constants of the motion, there is only one state of equilibrium. In contrast the number of non-equilibrium states is huge. In fact, the term "non-equilibrium state" is so indefinite as to be hardly less restrictive than "microscopic state." It is, nevertheless, a remarkable fact that a large and important class of processes can be adequately described in terms of a limited class of macroscopic variables. The variables referred to are such quantities as the mean local energy density, particle number density, momentum density, etc., or equivalently, the local thermodynamic variables: temperature, chemical potential, velocity, etc. Processes which can be described in terms of these variables are called hydrodynamic. (We use the term hydrodynamic in a general sense, without meaning to imply that a particular set of equations, such as the Navier–Stokes equations, are applicable. A more precise meaning of the term will be given in Section XII.)

Our purpose here is to discuss the derivation, from the principles of statistical mechanics, of the hydrodynamical equations of motion. We will adopt a purely formal point of view, and consequently will not become involved with the many-body problem, which is of course an important area of the theory of nonequilibrium phenomena.

The equations of hydrodynamics can be divided into two classes, the conservation laws and the transport relations. As an example, consider heat conduction. Conservation of energy is expressed by

$$\partial u/\partial t + \nabla \cdot \mathbf{s} = 0 \tag{1}$$

where u is the energy density and $\mathbf{s}$ the energy flux. The transport relation connects the energy flux to the temperature, and in many situations one may apply the Fourier law

$$\mathbf{s} = -\lambda \nabla T \tag{2}$$

where λ is the thermal conductivity and T the temperature. Equations (1) and (2), with u given as a function of T, provide a complete description of the heat flow. In more general circumstances there is a similar division of the hydrodynamic equations into conservation laws such as (1), plus transport relations such as (2).

The conservation laws are a reflection, on the macroscopic scale, of certain microscopic identities, also called conservation laws. The latter are presumed to be exact, and of course are not restricted to hydrodynamic processes. We will suppose the microscopic conservation laws to be given, as their derivation is primarily a matter for microscopic physics rather than statistical mechanics. Derivations have been discussed by a number of authors, including Hill,[10], Wentzel,[25] Irving and Kirkwood,[11] and Eisenschitz.[7]

Such quantities as $\mathbf{s}$ and u are, on the microscopic scale, quite independent except for the restriction imposed by the conservation laws. Consequently the transport relations, in contrast to the conservation laws, can hold only under special conditions. (Such conditions are implied in the term hydrodynamic, since all macroscopic quantities must depend on the local thermodynamic variables only.) Thus the main problem in a derivation of the hydrodynamic equations has to do with the transport relations rather than the conservation laws, and in particular it is necessary to somehow characterize the conditions which lead to hydrodynamic behavior.

The most extensively developed theory of transport processes is that based on the Boltzmann equation. This approach is, however, mainly restricted to a dilute gas of point molecules. In recent years, a number of authors have been concerned with a more general approach to transport theory. Of those pertinent here, the first is that of Green,[9] who applied the theory of Markoff random processes to hydrodynamics and obtained certain exact formal expressions for such transport coefficients as the thermal conductivity, viscosity, and coefficients of diffusion. These expressions have the form of a time integral of time-dependent correlation functions of microscopic fluxes, the correlation functions being evaluated for thermodynamic equilibrium. (Similar, but approximate, formulae had been obtained earlier by Kirkwood.[12]) Green's results have also been obtained by Kubo, Yokota and Nakajima[14] whose work is based on Onsager's assumption regarding the regression of fluctuations, and by Mori[20] using a method based on time-smoothing.

The above discussions are all concerned with the approach to equilibrium of an isolated system. The method to be used here, which has been discussed in earlier papers by the author[18] and is similar in its point of view to the work of Lebowitz and Bergmann,[16] is based on the explicit introduction of the external forces which bring about a deviation from equilibrium. These forces are assumed to arise from interaction with surroundings which can be characterized thermodynamically, and the solution of the resulting Liouville equation yields a Gibb's ensemble which is appropriate to hydrodynamics and which is therefore analogous to the "normal" solution to the Boltzmann equation. The transport relations are then obtained by an approximation procedure which closely resembles that of Chapman and Enskog.[5] This approach has the practical advantage of providing, at least in principle, a completely general description of hydrodynamics, while in contrast the work cited in the previous paragraph has been restricted to slowly varying processes, near equilibrium.

The behavior of a system interacting with an external electromagnetic field has been discussed by Callen and Welton.[4] Subsequently Kubo,[13] Landau and Lifshitz,[15] and others obtained a formula for electrical conductivity which is of the same type as the Green formulae for the other transport coefficients. Our approach is similar to that of these authors insofar as it is based on the consideration of external forces, but, as will be seen, there is a basic difference between electrical and non-electrical processes.

As already mentioned we will be concerned only with a formal description of transport processes. Such a description must be supplemented by the development of practical approximation methods for the evaluation of the transport coefficients. Considerable progress toward the solution of this problem has been made with the aid of many-body methods such as those developed by van Hove[23] and Prigogine.[21] Discussions which deal particularly with the evaluation of transport coefficients have been given by Chester and Thellung,[6] Montroll and Ward,[19] Fujita and Abe,[8] and Balescu.[1] In addition we refer to the Green's function approach as developed by Martin and Schwinger[17] and others cited by them. It should be remarked that in the following we will make certain assumptions concerning the asymptotic behavior of correlation functions, and these can be rigorously justified only by detailed microscopic arguments of the sort used in the above references.

II. LIOUVILLE EQUATION FOR A NON-ISOLATED SYSTEM

As remarked in the Introduction our method is to generate a non-equilibrium state through the introduction of external forces. Therefore our first task concerns the statistical mechanics of a system interacting with its surroundings. These surroundings will be assumed to consist of reservoirs which can exchange energy and particles with the system, and mechanical devices which set up a momentum flow. It is important that the surroundings be controllable in the sense that their temperature, chemical potential, and velocity are forced to take on certain values independently of the processes occurring in the system.

We consider first a classical system; quantum mechanical effects will be taken into account in Section XI. Assume the system and surroundings together form a closed system which we will refer to as the universe. Let the hamiltonian for the universe be separated according to

$$H_u = H + H_s + V \tag{3}$$

where H is the hamiltonian for the system alone, H_s that for the surroundings, and V the interaction, which will be assumed to be independent of the momentum variables. A Gibbs ensemble for the universe is described by a distribution function ρ satisfying the Liouville equation

$$\partial\rho/\partial t + \{\rho,H_u\} = 0 \tag{4}$$

where the brackets $\{\}$ represent the Poisson bracket. An ensemble for the universe automatically entails one for the system and surroundings separately, according to

$$f = \int d\psi\, \rho, \qquad g = \int d\varphi\, \rho \tag{5}$$

Here the integrations are taken over that part of the phase space referring to the surroundings and to the system respectively, $d\psi$ and $d\varphi$ being the corresponding elements of volume. If ρ is normalized, it follows immediately that f and g are also normalized,

$$\int d\varphi\, f = 1, \qquad \int d\psi\, g = 1 \tag{6}$$

If X is defined by

$$\rho = fgX \tag{7}$$

then $X - 1$ is a measure of the statistical correlation between the system and surroundings. If $X = 1$, the system and surroundings are uncorrelated.

A Liouville equation for f can be obtained by integration of Eq. (4) over the phase space of the surroundings. One finds

$$\partial f/\partial t + \{f,H\} + \int d\psi\, \{\rho,H_s\} + \int d\psi\, \{\rho,V\} = 0 \tag{8}$$

The integrand in the third term above is a divergence in the phase space of the surroundings, and the integral vanishes if ρ is assumed to vanish sufficiently rapidly in the remote regions of phase space The last term may be transformed to give

$$\partial f/\partial t + \{f,H\} + \partial f F_\alpha/\partial p_\alpha = 0 \tag{9}$$

where

$$F_\alpha = -\int d\psi\, g X \partial V/\partial q_\alpha \tag{10}$$

Here the q_α and p_α are the coordinates and momenta of the system, and we have used the summation convention that terms containing repeated indices are to be summed.

The F_α are effective external forces representing the effect of the surroundings on the system. They depend on the statistical state of the universe, and in general are functions of the time and the momentum variables, and are non-conservative. If however $X = 1$, that is, if the system and surroundings are uncorrelated, the forces are conservative,

$$F_\alpha = -\frac{\partial}{\partial q_\alpha}\int d\psi\, g V, \tag{11}$$

and they can be represented by an addition to the system's hamiltonian.

An important distinction arises between forces of an electromagnetic and of a non-electromagnetic nature. The former are long-ranged and as a consequence the sources of the electromagnetic field can be assumed to be spatially separated from the system. Under such conditions the correlations between the system and the sources can be neglected and the effect of the sources described in terms of a prescribed macroscopic field. Such a field can be included in the hamiltonian in a well-known way. In contrast the forces giving rise to, say, a temperature gradient are short-ranged: a thermal reservoir is effective only if located close to the boundaries of the system. Strong correlations are set up in the region adjacent to the boundaries, and these have the effect that the forces are non-conservative and cannot be described by the hamiltonian formalism. (If the forces F_α are to be included in the hamiltonian, it is necessary that $\partial F_\alpha/\partial p_\alpha = 0$. However, it will be seen that it is precisely the non-vanishing of $\partial F_\alpha / \partial p_\alpha$ which leads to such phenomena as heat conduction.)

That the non-electromagnetic forces are non-conservative can easily be seen directly. A system interacting with an external time-independent conservative force must, with the passage of time, approach an equilibrium state characterized by a hamiltonian in which the external interaction is included. However, a time-independent force giving rise to, say, a temperature gradient leads not to equilibrium but to a dissipative steady state. (It is of course possible that the interaction with a thermal reservoir may have a conservative part, corresponding to conservative wall forces. However, we will suppose such a part, at least insofar as it is time-independent, to be included in the hamiltonian H.)

The distinction between electrical and non-electrical processes has another aspect. An external electric field can induce an electric current, and the calculation of this response, as in Kubo's theory, leads to the formula for electric conductivity. In contrast a heat current, for example, is the response to an internal temperature gradient and depends only indirectly on the external forces which set up this temperature gradient.

It will be noted that the procedure used in obtaining Eq. (9) is identical with that followed in obtaining the hierarchy of equations of Bogoliubov,[2] Born and Green,[3] Kirkwood,[12] and Yvon.[27] There, however, the concern is with a distribution function f of low order, referring to one or a small number of molecules, while here the system of interest is of macroscopic size. Actually Eq. (9) could have been written down immediately, since it is known to be the form of the Liouville equation in the presence of non-conservative forces. (Cf. the discussion by Whitaker[26] on integral invariants.)

If $\partial F_\alpha / \partial p_\alpha \neq 0$, then $f = 1$ is not a solution to the Liouville equation (9). Consequently the principle of equal *a priori* probabilities is not valid, in the system phase space. This is not surprising: equal volumes in the phase space for the universe do not project onto equal volumes in a subspace. In the past there have been some attempts to describe the non-equilibrium steady state by a procedure similar to that used for equilibrium, that is, by treating the steady state as a state of maximum probability subject to, say, a prescribed temperature gradient. While such a procedure may be legitimate, it is essential that the non-equality of the *a priori* probabilities be taken into account.

It is convenient to write Eq. (9) in terms of η, defined by

$$f = e^{\eta} \tag{12}$$

We then have

$$\partial\eta/\partial t + \{\eta,H\} + F_{\alpha}\partial\eta/\partial p_{\alpha} + \partial F_{\alpha}/\partial p_{\alpha} = 0 \tag{13}$$

In the presence of the external forces F_{α}, the time dependence of a function of t, q_{α}, and p_{α} is determined by

$$dA(t,q_{\alpha},p_{\alpha})/dt = \partial A/\partial t + \{A,H\} + F_{\alpha}\partial A/\partial p_{\alpha} \tag{14}$$

Hence Eq. (13) becomes

$$d\eta/dt = -\partial F_{\alpha}/\partial p_{\alpha} \tag{15}$$

III. SPECIFICATION OF THE EXTERNAL FORCES

To proceed further it is necessary to discuss the form of the external forces. In particular we wish to characterize these forces in some manner by the values of the thermodynamic variables, temperature, chemical potential, and velocity, associated with the surroundings. That such a characterization should be possible is indicated by experiment; in fact, a thermal reservoir is adequately described by its temperature, with the details of its structure and microscopic state being evidently unimportant.

We first show that if the surroundings consist of a number of independent reservoirs the forces F_{α} due to different reservoirs are additive. Write the ensemble for the universe as

$$\rho = f\textstyle\prod_r g_r X_r \tag{16}$$

where the subscript r labels different reservoirs. Here g_r is the ensemble for the rth reservoir and X_r describes the correlation between the rth reservoir and the system. Thus g_r depends only on the variables referring to the rth reservoir, while X_r depends in addition on the system variables. In writing X as a product as in Eq. (16) we have assumed that there are no direct statistical correlations between two different reservoirs, that is, that different reservoirs are statistically independent. Normalization of ρ, f, and the g_r requires

$$\int d\psi_r\, g_r X_r = 1 \tag{17}$$

where the integration extends over the phase space for reservoir r. The potential V may be written

$$V = \sum_r V_r \tag{18}$$

and hence

$$F_\alpha = -\int d\psi \textstyle\prod_{r'} g_{r'} X_{r'} \sum_r \partial V_r / \partial q_\alpha \tag{19}$$

For fixed r the integration above may be carried out over those variables referring to reservoirs with $r' \neq r$, and the result evaluated from Eq. (17). One then finds

$$F_\alpha = \sum_r F_\alpha^r \tag{20}$$

with

$$F_\alpha^r = -\int d\psi_r\, g_r X_r \partial V_r / \partial q_\alpha \tag{21}$$

To relate the forces to the thermodynamic parameters of the surroundings we consider first the interaction with a single thermal reservoir, and assume this interaction to be such that the system can reach an equilibrium state at a temperature equal to that of the reservoir. Suppose this equilibrium state to be described by a canonical ensemble

$$f_r = \exp\,(\alpha_r - \beta_r H) \tag{22}$$

where $T_r = 1/k\beta_r$ is the Kelvin temperature of the reservoir, k is Boltzmann's constant, and α_r is determined by normalization of f_r,

$$\exp\,(-\alpha_r) = \int d\varphi \exp\,(-\beta_r H) \tag{23}$$

Requiring that f_r be a solution to Eq. (9) (with only the forces F_α^r due to the single reservoir being included) yields the condition

$$\partial F_\alpha^r / \partial p_\alpha = \beta_r F_\alpha^r \partial H / \partial p_\alpha \tag{24}$$

This is just β_r times the rate of change of the system's energy, due to the external interaction,

$$\partial F^r_\alpha / \partial p_\alpha = \beta_r (dH/dt)_r \tag{25}$$

In the presence of more than one reservoir we obtain (denoting the total force due to all reservoirs by F_α)

$$\partial F_\alpha / \partial p_\alpha = \sum_r \beta_r (dH/dt)_r \tag{26}$$

Equation (26) actually involves an additional assumption. The external forces depend, through the quantity X, on the correlation between system and surroundings, and one may expect this correlation to change as the state of the system changes. Thus it is possible that the relation (25) may no longer hold if the system is not in equilibrium. However, we assume this not to be the case, that is, we treat the F_α as *prescribed* forces whose form is given independently of the statistical state of the system. Such an assumption may not in all respects accurately reproduce the properties of an actual reservoir. However, in the present context it is legitimate for the following reason. We will later, in accordance with an important property of actual reservoirs, assume the external forces to act only in the neighborhood of the boundary of the system. Transport processes in the interior of the system will depend only on the local thermodynamic variables, and must be independent of the detailed form of the distant external forces which bring about the deviation from equilibrium. Thus, so far as hydrodynamic processes are concerned, one may within wide limits choose any form for the external interaction, and the choice (26) is justified by convenience.

We will wish to consider time-dependent situations, and we assume that the time-dependence of the external forces can be adequately taken into account with a time-dependent temperature. That is, we assume Eq. (26) to hold even when the β_r depend on the time.

Equation (26) gives the desired connection between the external forces and the temperatures of the surrounding reservoirs. The forces are not completely determined by this relation, but a more detailed specification is not needed for our purposes. We note that an argument similar to the above was first used by

Lebowitz and Bergmann[16] to obtain a restriction on their reservoir interactions.

Consider next a more general situation. Suppose the system to interact with a single reservoir which may exchange particles as well as energy, and which in addition is in a state of uniform motion. We assume the interaction to be such that the system can exist in a state of equilibrium with a temperature, chemical potential, and velocity equal to those of the reservoir. An ensemble corresponding to these conditions is given by

$$f_r = \exp\left[-q_r - \beta_r H + (\nu_r - \tfrac{1}{2}\beta_r m v_r^2)N + \beta_r \mathbf{v}_r \cdot \mathbf{P}\right] \tag{27}$$

Here $\nu_r = \beta_r \mu_r$, where μ_r is the chemical potential of the reservoir, N is the total number of particles in the system, $\mathbf{v}_r$ the velocity of the reservoir, $\mathbf{P}$ the total momentum of the system, q_r is determined by normalization,

$$\exp q_r = \sum_N \frac{1}{N!} \int d\varphi \exp\left[-\beta_r H + (\nu_r - \tfrac{1}{2}\beta_r m v_r^2)\, N + \beta_r \mathbf{v}_r \cdot \mathbf{P}\right] \tag{28}$$

and m is the mass of a particle.

We have supposed there to be only one kind of particle; in the presence of a variety of particles the term $\nu_r N$ is replaced by a sum of such terms, one for each kind.

The ensemble (27) is readily obtained by transforming the usual grand canonical ensemble to a moving coordinate system. In making this transformation we have neglected relativistic effects; the hamiltonian H then transforms according to

$$H \rightarrow H - \mathbf{v}_r \cdot \mathbf{P} + \tfrac{1}{2} N m v_r^2 \tag{29}$$

On repeating the argument which gave Eq. (26), but using the ensemble (27) rather than (22), one now finds

$$\partial F_\alpha / \partial p_\alpha = \sum_r [\beta_r (dH/dt)_r - (\nu_r - \tfrac{1}{2}\beta m v_r^2)(dN/dt)_r - \beta_r \mathbf{v}_r \cdot (d\mathbf{P}/dt)_r] \tag{30}$$

The above comments concerning Eq. (26) also apply here.

There is a certain difficulty connected with the interpretation of Eq. (30) in classical mechanics, since N is usually treated as a fixed number rather than a dynamical variable. In addition, the interaction giving rise to a particle flow can clearly not be described in terms of forces. This difficulty does not arise in the second-quantization formalism of quantum mechanics, and consequently we will ignore it here, simply assuming that the expression $(dN/dt)_r$ and the corresponding "forces" can be given a suitable meaning.

IV. CONTINUOUS SYSTEMS

Our next task is to write the above results, particularly Eq. (30), in terms of the variables appropriate to a continuous system. Considering first an isolated system, we suppose the microscopic equations of motion to admit the conservation laws

$$\begin{aligned} \partial n/\partial t + \nabla \cdot \mathbf{j} &= 0 \\ \partial u/\partial t + \nabla \cdot \mathbf{s} &= 0 \\ \partial p_i/\partial t + \partial t_{ij}/\partial x_j &= 0 \end{aligned} \tag{31}$$

Here n, u, and $\mathbf{p}$ are the densities of particle number, energy, and momentum, and $\mathbf{j}$, $\mathbf{s}$, and t_{ij} their corresponding fluxes. The densities and fluxes are functions of the space coordinates x_i and of the q_α, p_α, but this dependence will not be explicitly indicated except where necessary to avoid confusion. For a multicomponent fluid one can introduce quantities n^k, $\mathbf{j}^k$ for each component, and in the absence of chemical reactions there is a conservation law for each component

$$\partial n^k/\partial t + \nabla \cdot \mathbf{j}^k = 0 \tag{32}$$

The total particle number, energy, and momentum are given by

$$\begin{aligned} N &= \sum_k N^k, \qquad N^k = \int dv\, n^k \\ H &= \int dv\, u \\ \mathbf{P} &= \int dv\, \mathbf{p} \end{aligned} \tag{33}$$

the integration extending over the volume of the system.

The stress tensor t_{ij} may be assumed to be symmetric,

$$t_{ij} = t_{ji} \tag{34}$$

In addition, for the energies of usual interest the momentum density and particle flux are simply related; for a one-component medium one has

$$\mathbf{p} = m\mathbf{j} \tag{35}$$

For a multicomponent system this becomes

$$\mathbf{p} = \sum_k m^k \mathbf{j}^k \tag{36}$$

However, the relations (35) and (36) do not apply at relativistic energies, since $\mathbf{p}$ and $\mathbf{j}$ have different transformation properties under a Lorentz transformation.

The conservation laws applying to a particular system may, in some cases, differ from (31). However, we will restrict our attention to (31), which provides a typical, and important, example.

We will suppose the boundaries of the system to be defined by perfectly reflecting walls. In the neighborhood of such a boundary there can be no flux of particles or energy in the normal direction,

$$\mathbf{n} \cdot \mathbf{j} = 0, \qquad \mathbf{n} \cdot \mathbf{s} = 0 \quad \text{(at the boundary)} \tag{37}$$

Here $\mathbf{n}$ is a unit vector normal to the boundary. In addition, there can be no flux in the normal direction of a tangential component of momentum, or

$$e_i n_j t_{ij} = 0 \quad \text{(at the boundary)} \tag{38}$$

where $\mathbf{e}$ is a unit vector normal to $\mathbf{n}$. There is, however, a flux in the normal direction of the normal component of momentum, due to the force exerted by the wall,

$$n_i n_j t_{ij} \neq 0 \tag{39}$$

We emphasize that the conservation laws (31) are identities: if the fluxes and densities are expressed as functions of the q_α, p_α, and the time dependence of the latter determined by the microscopic equations of motion, then the left-hand sides of the conservation laws reduce identically to zero. Stated differently, if the time derivatives are replaced by Poisson brackets, the resulting equations

$$\begin{aligned} \{n,H\} + \nabla \cdot \mathbf{j} &= 0 \\ \{u,H\} + \nabla \cdot \mathbf{s} &= 0 \\ \{p_i,H\} + \partial t_{ij}/\partial x_j &= 0 \end{aligned} \tag{40}$$

hold identically in the q_α, p_α.

If the interparticle interactions take place via instantaneous forces the fluxes $\mathbf{s}$ and t_{ij} are non-local, that is, $\mathbf{s}(x)$ and $t_{ij}(x)$ depend on conditions throughout a neighborhood around the point x. The extent of this non-locality is of the order of the force range, which in most cases is negligibly small.

The fluxes are not unique, since one can always add to them a quantity with vanishing divergence without affecting the conservation laws. Actually, we have tacitly restricted this arbitrariness to some extent in Eqs. (35) through (38). We will impose additional restrictions by requiring that the fluxes depend on the time only through their dependence on the q_α, p_α, and that their coordinate dependence occurs only in the combinations $q_{\alpha i} - x_i$. These requirements may be expressed by

$$\partial F/\partial t = \{F,H\}, \qquad \partial F/\partial x_i = -\{F,P_i\} \tag{41}$$

where F is any one of the fluxes. This has the effect of eliminating a possible divergenceless term which depends only on x_i and t. It may be verified that the restrictions imposed here are actually satisfied by the "usual" form of the fluxes as given by, for example, Irving and Kirkwood.[11]

Consider next the modification of the conservation laws when an interaction with the surroundings is introduced. We will take the densities and fluxes to be the same functions of the q_α, p_α as for an isolated system. The meaning of the time derivative is, however, altered by a contribution from the external forces, and we write

$$\begin{aligned} \partial n/\partial t + \nabla \cdot \mathbf{j} &= c \\ \partial u/\partial t + \nabla \cdot \mathbf{s} &= w \\ \partial p_i/\partial t + \partial t_{ij}/\partial x_j &= f_i \end{aligned} \tag{42}$$

Here c is the particle source density, w the rate at which work is done per unit volume by the external forces, and $\mathbf{f}$ the force per unit volume. Equations (42) are actually the definitions of their right-hand sides. The external forces, and consequently the sources c, w, and $\mathbf{f}$, will be assumed to vanish except in a region near the boundary of the system. Assuming the external forces to be distributed in some continuous manner, one may rewrite Eq. (30) as

$$\partial F_\alpha/\partial p_\alpha = \int dv\, \{\beta(x,t)w(x,t) - [\nu(x,t) - \tfrac{1}{2}m\beta(x,t)v^2(x,t)]c(x,t) \\ - \beta(x,t)\mathbf{v}(x,t)\cdot\mathbf{f}(x,t)\} \tag{43}$$

Here $\beta(x,t)$, $\nu(x,t)$, and $\mathbf{v}(x,t)$ are the thermodynamic parameters associated with the reservoir acting at point x, and a possible time dependence of these parameters has been included. (Note that the sources c, w, and $\mathbf{f}$ may be explicitly time-dependent, since they arise from the action of forces which may be time-dependent. On the other hand the densities and fluxes do not depend explicitly on the time.)

Use of Eq. (42) enables one to rewrite Eq. (43) as

$$\begin{aligned}\frac{\partial F_\alpha}{\partial p_\alpha} = \frac{d}{dt}\int dv\, \{&\beta(x,t)u(x) - [\nu(x,t) - \tfrac{1}{2}m\beta(x,t)v^2(x,t)]n(x) \\ &- \beta(x,t)\mathbf{v}(x,t)\cdot\mathbf{p}(x)\} \\ &- \int dv\, \Big\{u(x)\,\frac{\partial\beta(x,t)}{\partial t} - n(x)\,\frac{\partial}{\partial t}[\nu(x,t) - \tfrac{1}{2}m\beta(x,t)v^2(x,t)] \\ &- \mathbf{p}(x)\cdot\frac{\partial}{\partial t}\beta(x,t)\mathbf{v}(x,t) - \beta(x,t)\nabla\cdot\mathbf{s}(x) \\ &+ [\nu(x,t) - \tfrac{1}{2}m\beta(x,t)v^2(x,t)]\nabla\cdot\mathbf{j}(x) + \beta(x,t)v_i(x,t)\,\frac{\partial t_{ij}(x)}{\partial x_j}\Big\}\end{aligned}$$

We next integrate by parts, assuming that in the neighborhood of the boundary $\mathbf{v}(x)$ is tangential to the boundary. (Otherwise the boundary could not remain fixed.) The surface integral resulting from the integration by parts then vanishes as a consequence of Eqs. (37) and (38) and one finds

$$\begin{aligned}\frac{\partial F_\alpha}{\partial p_\alpha} = \frac{d}{dt}\int dv\, \{&\beta(x,t)u(x) - [\nu(x,t) - \tfrac{1}{2}m\beta(x,t)v^2(x,t)]n(x) \\ &- \beta(x,t)\mathbf{v}(x,t)\cdot\mathbf{p}(x)\} \\ &- \int dv \left\{\mathbf{s}(x)\cdot\nabla\beta(x,t) + u(x)\,\frac{\partial\beta(x,t)}{\partial t}\right. \\ &- \mathbf{j}(x)\cdot\nabla[\nu(x,t) - \tfrac{1}{2}m\beta(x,t)v^2(x,t)] \qquad (44) \\ &- n(x)\,\frac{\partial}{\partial t}[\nu(x,t) - \tfrac{1}{2}m\beta(x,t)v^2(x,t)] \\ &\left. - t_{ij}(x)\,\frac{\partial}{\partial x_j}\,\beta(x,t)v_j(x,t) - \mathbf{p}(x)\cdot\frac{\partial}{\partial t}\,\beta(x,t)\mathbf{v}(x,t)\right\}\end{aligned}$$

V. THE NON-EQUILIBRIUM ENSEMBLE

Equations (15) and (44) yield an equation for the determination of η. To simplify the algebra we first consider only those terms descriptive of heat flow and obtain

$$\frac{d\eta}{dt} = -\frac{d}{dt}\int dv\,\beta(x,t)u(x) + \int dv\left[\mathbf{s}(x)\cdot\nabla\beta(x,t) + u(x)\,\frac{\partial\beta(x,t)}{\partial t}\right] \qquad (45)$$

This equation has many solutions, since one can always add a solution to the homogeneous equation

$$d\eta/dt = 0 \qquad (46)$$

To obtain a particular solution we will impose an initial condition. We assume that at $t = -\infty$ the system is in equilibrium and is described by a grand canonical ensemble,

$$\eta(t = -\infty) = -q - \beta H + \nu N \qquad (47)$$

Here $1/k\beta$ is the initial temperature, ν/β the initial chemical potential, and q is determined by normalization,

$$\exp q = \sum_N \frac{1}{N!}\int d\varphi\, \exp\,(\nu N - \beta H) \qquad (48)$$

The initial condition (47) corresponds to the usual situation: one begins with a system in equilibrium, or nearly so, and brings it to the desired non-equilibrium state by external interaction. It is of course not necessary to impose the initial condition at an infinite time, since the external forces could be assumed to vanish from $t = -\infty$ until some finite time.

To obtain a formal solution to Eq. (45) let A be any function of q_α, p_α and denote by $A(t',t)$ a solution to the equations of motion with the external forces included:

$$\begin{gathered}\partial A(t',t)/\partial t + \{A(t',t), H\} + F_\alpha(t)\partial A(t',t)/\partial p_\alpha = 0 \\ A(t,t) = A\end{gathered} \tag{49}$$

It may then be verified that the solution to Eq. (45) which satisfies the initial condition (47) is given by

$$\begin{aligned}\eta(t) = {} & -q - \int dv\ \beta(x,t)u(x) + \nu N \\ & + \int_{-\infty}^{t} dt' \int dv\ [\mathbf{s}(x,t',t) \cdot \nabla\beta(x,t') + u(x,t',t)\partial\beta(x,t')/\partial t']\end{aligned} \tag{50}$$

Here we have assumed that $\beta(x,t)$ approaches the constant β as $t \to -\infty$ sufficiently rapidly to ensure convergence of the time integral.

The ensemble f is given by $f = \exp \eta$, which we write as

$$f = f_L e^D \tag{51}$$

where

$$f_L = \exp[-q(t) - \int dv\ \beta(x,t)u(x) + \nu N] \tag{52}$$

$$\begin{aligned}D = q(t) - q + \int_{-\infty}^{t} dt' \int dv\ [\mathbf{s}(x,t',t) \cdot \nabla\beta(x,t') \\ + u(x,t',t)\partial\beta(x,t')/\partial t']\end{aligned}$$

The quantity $q(t)$ will be determined below in such a way as to normalize f_L. (Note that f is normalized, since it is a solution to a Liouville equation which preserves normalization, and the initial ensemble (47) is normalized.)

For the more general case, with all terms of Eq. (44) taken into account, one finds

$$f_L = \exp\Big\{-q(t) + \int dv\,[-\beta(x,t)u(x) + [\nu(x,t) - \tfrac{1}{2}m\beta(x,t)v^2(x,t)]n(x) + \beta(x,t)\mathbf{v}(x,t)\cdot\mathbf{p}(x)]\Big\} \tag{53}$$

$$\begin{aligned} D = q(t) - q + \int_{-\infty}^{t} dt' \int dv \Big\{ &\mathbf{s}(x,t',t)\cdot\nabla\beta(x,t') + u(x,t',t)\,\partial\beta(x,t')/\partial t' \\ &- \mathbf{j}(x,t',t)\cdot\nabla[\nu(x,t') - \tfrac{1}{2}m\beta(x,t')v^2(x,t')] \\ &- n(x,t',t)\frac{\partial}{\partial t'}[\nu(x,t') - \tfrac{1}{2}m\beta(x,t')v^2(x,t')] \\ &- t_{ij}(x,t',t)\frac{\partial}{\partial x_j}\beta(x,t')v_i(x,t') - \mathbf{p}(x,t',t)\cdot\frac{\partial}{\partial t'}\beta(x,t')\mathbf{v}(x,t')\Big\} \end{aligned} \tag{54}$$

We note that D, and consequently the ensemble f, are unchanged if the fluxes are altered by divergenceless additions, provided that the conditions (37) and (38) are maintained.

VI. LOCAL EQUILIBRIUM

The factor f_L has been separated off since it provides a description of "local equilibrium." Assume the system can be divided into volume elements which are large enough for statistical correlations between them to be neglected, but are yet small enough for the variations in the parameters $\beta(x,t)$, $\nu(x,t)$ and $\mathbf{v}(x,t)$ over one element to be small. Then f_L describes a situation such that a volume element located at point x is distributed canonically with a temperature $T(x,t) = 1/k\beta(x,t)$, chemical potential $\mu(x,t) = \nu(x,t)/\beta(x,t)$, and velocity $\mathbf{v}(x,t)$. (Actually we still have to justify the use of the names temperature, chemical potential, and velocity.) The calculation of averages with respect to f_L is thus essentially an equilibrium calculation, and is easily done.

For short-range intermolecular forces the distance over which correlations are appreciable is of the order of the force range, which is negligibly small in most cases of interest. However, large correlation distances can be induced by the long-range electromagnetic field and a different treatment, which will be given in Section X, is then necessary.

We first determine the quantity $q(t)$, and then obtain the local equilibrium averages for the various quantities of interest. Normalization of f_L requires that

$$\exp q(t) = \sum_N \frac{1}{N!} \int d\varphi \exp \int dv \,\{-\beta(x,t)u(x) + [\nu(x,t) - \tfrac{1}{2}m\beta(x,t)v^2(x,t)]n(x) + \beta(x,t)\mathbf{v}(x,t)\cdot\mathbf{p}(x)\} \tag{55}$$

On taking the time derivative one finds

$$\frac{dq(t)}{dt} = \int dv \left\{-\langle u(x)\,;t\rangle_L \frac{\partial\beta(x,t)}{\partial t} + \langle n(x)\,;t\rangle_L \frac{\partial}{\partial t}[\nu(x,t) - \tfrac{1}{2}m\beta(x,t)v^2(x,t)] + \langle \mathbf{p}(x)\,;t\rangle_L \cdot \frac{\partial}{\partial t}\beta(x,t)\mathbf{v}(x,t)\right\} \tag{56}$$

where the brackets $\langle\,;t\rangle_L$ denote an average taken with $f_L(t)$. At time $t = -\infty$, $q(t) = q$ and hence

$$q(t) - q = \int_{-\infty}^{t} dt' \int dv \left\{-\langle u(x)\,;t'\rangle_L \frac{\partial\beta(x,t')}{\partial t'} + \langle n(x)\,;t'\rangle_L \frac{\partial}{\partial t'}[\nu(x,t') - \tfrac{1}{2}m\beta(x,t')v^2(x,t')] + \langle \mathbf{p}(x)\,;t'\rangle_L \cdot \frac{\partial}{\partial t'}\beta(x,t')\mathbf{v}(x,t')\right\} \tag{57}$$

To calculate the average of a quantity localized at the point x it is convenient to perform a Galilean transformation to a coordinate system moving with the velocity $\mathbf{v}(x,t)$; the volume element at x then appears to be at rest. Under such a transformation the densities and fluxes transform according to (for simplicity we drop the arguments x,t)

$$\begin{aligned} n &= n' \\ \mathbf{j} &= \mathbf{j}' + n'\mathbf{v} \\ u &= u' + \mathbf{p}' \cdot \mathbf{v} + \tfrac{1}{2}n'mv^2 \\ s_i &= s_i' + (u' + \tfrac{1}{2}n'mv^2 + \mathbf{p}' \cdot \mathbf{v})v_i + \tfrac{1}{2}v^2 p_i' + t_{ij}'v_j \\ \mathbf{p} &= \mathbf{p}' + n'm\mathbf{v} \\ t_{ij} &= t_{ij}' + v_i p_j' + v_j p_i' + n'mv_i v_j \end{aligned} \tag{58}$$

Here the primes denote quantities referring to the moving coordinate system. The above transformation laws (as well as the local equilibrium averages to be obtained) have been given by Green,[9] and may be obtained directly from the explicit form of the densities and fluxes.

With the aid of Eqs. (58) the local equilibrium averages are reduced to equilibrium averages for a system at rest. The averages of $\mathbf{j}'$, $\mathbf{p}'$, and $\mathbf{s}'$ must then vanish, while t_{ij}' yields the scalar pressure. We use the notation

$$\begin{aligned} n_e(x,t) &= n_e[\beta(x,t), \nu(x,t)] \\ u_e(x,t) &= u_e[\beta(x,t), \nu(x,t)] \\ p(x,t) &= p[\beta(x,t), \nu(x,t)] \end{aligned} \tag{59}$$

where $n_e(\beta,\nu)$, $u_e(\beta,\nu)$, and $p(\beta,\nu)$ are the equilibrium density, energy density, and pressure for a system at rest. One then finds (again dropping the arguments x,t)

$$\begin{aligned} \langle n(x);t\rangle_L &= n_e \\ \langle \mathbf{p}(x);t\rangle_L &= \rho\mathbf{v} \\ \langle u(x);t\rangle_L &= u_e + \tfrac{1}{2}\rho v^2 \end{aligned} \tag{60}$$

and

$$\begin{aligned} \langle \mathbf{s}(x);t\rangle_L &= (u_e + p + \tfrac{1}{2}\rho v^2)\mathbf{v} \\ \langle \mathbf{j}(x);t\rangle_L &= n_e\mathbf{v} \\ \langle t_{ij}(x);t\rangle_L &= \delta_{ij}p + \rho v_i v_j \end{aligned} \tag{61}$$

Here we have put

$$\rho = n_e m \tag{62}$$

For a multicomponent system we find

$$\begin{aligned} \langle n^k(x);t\rangle_L &= n_e^k \\ \langle \mathbf{j}^k(x);t\rangle_L &= n_e^k \mathbf{v} \end{aligned} \tag{63}$$

and Eq. (62) is replaced by

$$\rho = \sum_k n_e^k m^k \tag{64}$$

(The mass density ρ can be distinguished by context from the ensemble ρ introduced in Section II.)

Again we remark that the above results are valid only when the thermodynamic parameters $\beta(x,t)$, $\nu(x,t)$, and $\mathbf{v}(x,t)$ vary by negligible amounts over the distances for which correlations are important.

For later reference we use Eqs. (57) and (60) to write an alternative form for D,

$$\begin{aligned} D = \int_{-\infty}^{t} dt' \int dv \Big\{ &\mathbf{s} \cdot \nabla\beta + (u - u_e - \tfrac{1}{2}\rho v^2) \frac{\partial \beta}{\partial t'} \\ &- \mathbf{j} \cdot \nabla(\nu - \tfrac{1}{2}m\beta v^2) - (n - n_e) \frac{\partial}{\partial t'} (\nu - \tfrac{1}{2}m\beta v^2) \\ &- t_{ij} \frac{\partial}{\partial x_j} \beta v_i - (\mathbf{p} - \rho\mathbf{v}) \cdot \frac{\partial}{\partial t'} \beta\mathbf{v} \Big\} \end{aligned} \tag{65}$$

Here for simplicity we have dropped all arguments: the thermodynamic variables β, ν, $\mathbf{v}$, u_e, n_e, and ρ are to be evaluated at x,t', while the phase functions $\mathbf{s}$, u, $\mathbf{j}$, n, t_{ij}, and $\mathbf{p}$ have x, t', t as arguments.

VII. MACROSCOPIC CONSERVATION LAWS AND THERMODYNAMIC VARIABLES

In the previous Section we have anticipated the thermodynamic interpretation of $\beta(x,t)$, $\nu(x,t)$, and $\mathbf{v}(x,t)$, and this procedure must be justified. A related question concerns the macroscopic (or average) conservation laws.

As mentioned earlier, the external forces will be assumed to act only in a thin region near the boundary of the system. The forces will then vanish, and the conservation laws (31) will hold, in the interior of the system. Since the latter hold microscopically, that is for each member of the ensemble, they must hold on the average:

$$\begin{aligned}\partial\langle n(x);t\rangle/\partial t + \nabla\cdot\langle \mathbf{j}(x);t\rangle &= 0\\ \partial\langle u(x);t\rangle/\partial t + \nabla\cdot\langle \mathbf{s}(x);t\rangle &= 0\\ \partial\langle p_i(x);t\rangle/\partial t + \partial\langle t_{ij}(x);t\rangle/\partial x_j &= 0\end{aligned} \tag{66}$$

Here the brackets $\langle\,;t\rangle$ denote an average over the full ensemble $f(t)$. Since Eqs. (31) are identities, the above must also be identities. That is, if the mean densities and fluxes are completely calculated, the result will be certain functionals of the external forces, and Eqs. (66) must hold identically in these forces.

Consider now the definition of local temperature, chemical potential, and velocity for the non-equilibrium state. The velocity is clearly to be defined in terms of the mean momentum density according to

$$\langle \mathbf{p}(x);t\rangle = \langle n(x);t\rangle m\mathbf{v}(x,t) \tag{67}$$

We further define the local temperature and chemical potential by requiring that they be the same functions of the mean number density and (rest) energy density (which are mechanical quantities) as at equilibrium, or

$$\begin{aligned}\langle n(x);t\rangle &= n_e(x,t)\\ \langle u(x);t\rangle - \tfrac{1}{2}n_e(x,t)mv^2(x,t) &= u_e(x,t)\end{aligned} \tag{68}$$

Equations (67) and (68), in conjunction with Eqs. (60), clearly are equivalent to

$$\begin{aligned}\langle n(x);t\rangle &= \langle n(x);t\rangle_L\\ \langle u(x);t\rangle &= \langle u(x);t\rangle_L\\ \langle \mathbf{p}(x);t\rangle &= \langle \mathbf{p}(x);t\rangle_L\end{aligned} \tag{69}$$

Note that there is actually freedom to impose the conditions (69). The parameters $\beta(x,t)$, $\nu(x,t)$, and $\mathbf{v}(x,t)$ must take on the prescribed boundary values, but in the interior of the system they have been as yet completely arbitrary.

Equations (69) and (66) lead to

$$\begin{aligned} \partial\langle n(x);t\rangle_L/\partial t + \nabla\cdot\langle \mathbf{j}(x);t\rangle &= 0 \\ \partial\langle u(x);t\rangle_L/\partial t + \nabla\cdot\langle \mathbf{s}(x);t\rangle &= 0 \\ \partial\langle p_i(x);t\rangle_L/\partial t + \partial\langle t_{ij}(x);t\rangle/\partial x_j &= 0 \end{aligned} \tag{70}$$

On the other hand Eqs. (70) imply (69), since the identities (66) lead to

$$\begin{aligned} \frac{\partial}{\partial t}[\langle n(x);t\rangle - \langle n(x);t\rangle_L] &= 0 \\ \frac{\partial}{\partial t}[\langle u(x);t\rangle - \langle u(x);t\rangle_L] &= 0 \\ \frac{\partial}{\partial t}[\langle p_i(x);t\rangle - \langle p_i(x);t\rangle_L] &= 0 \end{aligned} \tag{71}$$

and in the infinite past, when the system is in equilibrium, Eqs. (69) hold. Thus, in view of the identities (66), Eqs. (69) and (70) are equivalent.

We emphasize the difference between Eqs. (66) and (70). The latter are what is usually meant by conservation laws in hydrodynamics. They are not identities, but in conjunction with the transport relations they form the hydrodynamic equations which determine the thermodynamic variables in terms of their prescribed boundary values. Thus the arbitrariness in the thermodynamic variables is removed by the conditions (69).

Clearly we are not obliged to determine the thermodynamic variables in the above manner, and it may therefore appear that the transport relations to be obtained below suffer from a lack of uniqueness. That this is not the case can be seen as follows. Equation (43) can be used in place of (44) to obtain the ensemble f in a form depending only on variables near the boundary. One could then in principle calculate the mean densities and their fluxes as certain functionals of the thermodynamic variables associated with the surroundings. The latter quantities could presumably be eliminated to obtain the transport relations, and this procedure is evidently unique. In other words, the transport relations, when expressed as connections between the fluxes and densities rather than between the fluxes and thermodynamic variables, must be unique. The above procedure would be quite impractical since it amounts to giving the *solution* to the hydrodynamic equations. These equations themselves are the desired goal, and hence the thermodynamic variables are extended into the interior of the system to provide an intermediary in the formulation of the transport relations. The particular extension determined by Eqs. (69) is dictated by the method of approximation to be used below. (We recall that in the kinetic theory of gases[5] the conditions (69) are necessary for the consistency of the Chapman–Enskog approximation method.)

The definition of thermodynamic variables adopted here has also been used by Green[9] and Mori,[20] and seems to be the most natural generalization of the equilibrium definitions. It should be noted, however, that there is a problem connected with the measurement of, say, the temperature for a non-equilibrium state. One is assured by the general principles of thermodynamics that a properly calibrated thermometer will always yield correct results in an equilibrium measurement. This is no longer true in a non-equilibrium situation. The result of a temperature measurement could depend on, say, the orientation of the thermometer with respect to the temperature gradient. However, we will simply dismiss this difficulty by taking the point of view that it concerns a matter of experimental practice. Note that there is really no difficulty in principle, since one could measure the mechanical quantities and invert Eqs. (67) and (68) to obtain the thermodynamic variables.

The above definitions can be extended to other local thermodynamic functions, such as the pressure, entropy density, specific heats, etc. Thus all intensive thermodynamic variables are, by definition, to be functionally related to the mean energy and number densities in the same way as at equilibrium. It then follows that the various thermodynamic identities derived by equilibrium arguments are still valid for the non-equilibrium state. (It is worth emphasizing that this procedure is quite general, and is not restricted to linear processes.)

The quantity $q(t)$ can now be given a simpler form. Taking into account Eq. (60) one can reduce Eq. (57) to

$$q(t) - q = \int_{-\infty} dt' \int dv \left[-u_e(x,t') \frac{\partial \beta(x,t')}{\partial t'} + n_e(x,t') \frac{\partial \nu(x,t')}{\partial t'} \right] \qquad (72)$$

The thermodynamic identity

$$\delta(\beta p) = -u_e \, \delta\beta + n_e \, \delta\nu \qquad (73)$$

yields

$$\begin{aligned} q(t) &= q + \int_{-\infty}^{t} dt' \int dv \frac{\partial}{\partial t'} \beta(x,t') p(x,t') \\ &= \int dv \, \beta(x,t) p(x,t) \end{aligned} \qquad (74)$$

which is of course expected from the fact that $q = \beta p \Omega$ in equilibrium, with Ω being the volume of the system.

VIII. ENTROPY PRODUCTION

In accordance with the remarks of the previous section we define entropy in terms of relations valid at equilibrium. Denoting the entropy density by $s(x,t)$ and using the thermodynamic identity

$$s = k[\beta(u_e + p) - \nu n_e] \qquad (75)$$

one finds for the total entropy S

$$\begin{aligned} S &= \int dv \, s(x,t) \\ &= k \int dv \, \{\beta(x,t)[u_e(x,t) + p(x,t)] - \nu(x,t) n_e(x,t)\} \end{aligned} \qquad (76)$$

In view of Eqs. (53), (60), and (74) this can be written as

$$S = -k \sum_N \frac{1}{N!} \int d\varphi \, f_L \ln f_L \qquad (77)$$

or, as a consequence of Eqs. (69),

$$S = -k \sum_N \frac{1}{N!} \int d\varphi \, f \ln f_L \qquad (78)$$

The time derivative of S is the internal entropy production,

$$\sigma_i = dS/dt \tag{79}$$

which can be determined from the hydrodynamic equations; to do this it is convenient to obtain a "conservation law" for s. Following a familiar argument one finds

$$\frac{\partial s}{\partial t} + \nabla \cdot s\mathbf{v} = k\beta \left[-\nabla \cdot \mathbf{s}^{\star} + v_i \frac{\partial t_{ij}^{\star}}{\partial x_j} \right] \tag{80}$$

For simplicity we have considered a single-component system, and have introduced the notation

$$\begin{aligned} \mathbf{s}^{\star}(x,t) &= \langle \mathbf{s}(x);t \rangle - \langle \mathbf{s}(x);t \rangle_L \\ t_{ij}^{\star}(x,t) &= \langle t_{ij}(x);t \rangle - \langle t_{ij}(x);t \rangle_L \end{aligned} \tag{81}$$

The contribution of f_L to the fluxes, as given by Eqs. (61), leads to hydrodynamic equations which describe a reversible process, and the irreversible contributions are therefore included in $\mathbf{s}^{\star}$ and $t_{ij}^{\star}$.

In obtaining Eq. (80) the conservation laws (70) have been used. Consequently Eq. (80) is valid only in the interior of the system. Near the boundary the sources must be included, and one then finds (for simplicity we neglect the source c)

$$\frac{\partial s}{\partial t} + \nabla \cdot s\mathbf{v} = k\beta \left[-\nabla \cdot \mathbf{s}^{\star} + \bar{w} + v_i \frac{\partial t_{ij}^{\star}}{\partial x_j} - \mathbf{v} \cdot \bar{\mathbf{f}} \right] \tag{82}$$

where

$$\bar{w}(x,t) = \langle w(x,t);t \rangle, \qquad \bar{\mathbf{f}}(x,t) = \langle \mathbf{f}(x,t);t \rangle \tag{83}$$

σ_i may now be determined by integrating Eq. (82) over the volume of the system; the contribution of the second term on the left-hand side can be changed to a surface integral which vanishes since $\mathbf{v}$ is tangential to the boundary. The result is

$$\sigma_i = k \int dv\, \beta[-\nabla \cdot \mathbf{s}^{\star} + \bar{w} + v_i \partial t_{ij}^{\star}/\partial x_j - \mathbf{v} \cdot \bar{\mathbf{f}}] \tag{84}$$

A quantity similar to S is

$$S' = -k \sum_N \frac{1}{N!} \int d\varphi\, f \ln f \tag{85}$$

To see the significance of S' we calculate its time derivative. Using the Liouville equation (9) one finds

$$dS'/dt = k \sum_N \frac{1}{N!} \int d\varphi \ln f \partial f F_\alpha / \partial p_\alpha \tag{86}$$

After two integrations by parts this becomes

$$\begin{aligned} dS'/dt &= k \sum_N \frac{1}{N!} \int d\varphi \, f \partial F_\alpha / \partial p_\alpha \\ &= k \langle \partial F_\alpha / \partial p_\alpha ; t \rangle \end{aligned} \tag{87}$$

and, with the aid of Eq. (43), one finds (recall that we are neglecting c)

$$dS'/dt = k \int dv \, \beta [\bar{w} - \mathbf{v} \cdot \bar{\mathbf{f}}] \tag{88}$$

This is just minus the entropy production in the external reservoirs:

$$dS'/dt = -\sigma_e \tag{89}$$

The total entropy production of the universe is

$$\sigma = \sigma_i + \sigma_e \tag{90}$$

By Eqs. (78) and (85) this is

$$\begin{aligned} \sigma &= -k \frac{d}{dt} \sum_N \frac{1}{N!} \int d\varphi \, f [\ln f_L - \ln f] \\ &= k \frac{d}{dt} \sum_N \frac{1}{N!} \int d\varphi \, f \ln (f/f_L) \\ &= k \frac{d}{dt} \sum_N \frac{1}{N!} \int d\varphi \, f D \end{aligned} \tag{91}$$

This shows the significance of the quantity D; the time derivative of its average is $1/k$ times the entropy production of the universe.

IX. TRANSPORT RELATIONS

The irreversible contributions to the fluxes are contained in the quantities $\mathbf{s}^\star$, $t^\star_{ij}$, and

$$\mathbf{j}^{\star k}(x,t) = \langle \mathbf{j}^k(x)\,;t\rangle - \langle \mathbf{j}^k(x)\,;t\rangle_L \tag{92}$$

(Note that for a system consisting of a single component $\mathbf{j}^\star$ vanishes as a consequence of Eqs. (35) and (69).) Clearly

$$\begin{aligned} \mathbf{j}^{\star k}(x,t) &= \langle \mathbf{j}^k(x)[e^D - 1]\,;t\rangle_L \\ \mathbf{s}^\star(x,t) &= \langle \mathbf{s}(x)[e^D - 1]\,;t\rangle_L \\ t^\star_{ij}(x,t) &= \langle t_{ij}(x)[e^D - 1]\,;t\rangle_L \end{aligned} \tag{93}$$

The transport relations (93) are generally valid. However, the connection between the fluxes and the thermodynamic variables is in general too complicated to be useful, and it is necessary to obtain simple approximations. We will consider an approximation method which is suited to ordinary fluids that can be described, at least for slowly varying processes, by the Navier–Stokes equations. For some systems, such as a viscoelastic medium, the Navier–Stokes equations are inadequate even as a first approximation, and the transport relations (93) must then be treated differently.

The discussion to follow has a close resemblance to the Chapman–Enskog approximation method in the kinetic theory of gases,[5] and it may be helpful to review briefly the basis of this method. The distribution function is expanded as

$$f = f^{(0)} + f^{(1)} + f^{(2)} + \cdots \tag{94}$$

and each term is chosen according to the space derivatives of the thermodynamic variables which appear in it. Thus $f^{(0)}$, which is identified with f_L, contains no derivatives, $f^{(1)}$ is linear in the first derivatives, $f^{(2)}$ linear in the second derivatives and quadratic in the first derivatives, etc. In this procedure, where time derivatives appear they are not to be considered as independent of the space derivatives, but are eliminated with the aid of the conservation laws. It is then necessary to obtain the mean fluxes, and at the rth stage of the approximation this is done with the aid of the previously determined $f^{(r-1)}$.

We will restrict our attention to linear processes for which the deviation from equilibrium is small, and the derivatives of the thermodynamic variables are then to be treated as small quantities. Thus second and higher powers of the derivatives are to be neglected, while derivatives of second and higher order may be retained. In addition, we will assume the local velocity, as well as its derivatives, to be small; this actually involves no loss in generality since one can always perform a Galilean transformation to bring any element of the fluid to rest.

If the deviation from equilibrium is assumed to be small not only at the time of observation but throughout the past history, D will be a small quantity, and hence

$$e^D - 1 = D + \cdots \tag{95}$$

Furthermore, in the linear approximation, Eq. (65) for D reduces to

$$\begin{aligned} D = \int_{-\infty}^{t} dt' \int dv\, \{ &\mathbf{s}(x,t',t) \cdot \nabla\beta(x,t') + [u(x,t',t) - u_e]\partial\beta(x,t')/\partial t' \\ &- \mathbf{j}(x,t',t) \cdot \nabla\nu(x,t') - [n(x,t',t) - n_e]\partial\nu(x,t')/\partial t' \\ &- \beta t_{ij}(x,t',t)\,\partial v_i(x,t')/\partial x_j - \beta\mathbf{p}(x,t',t) \cdot \partial\mathbf{v}(x,t')/\partial t'\} \end{aligned} \tag{96}$$

where variations in u_e, n_e, and β [as contrasted to $\beta(x, t)$] are to be ignored.

We consider first a simplified situation with vanishing local velocity and uniform pressure; the more general case will be treated later. For constant pressure the identities

$$(\partial p/\partial\nu)_\beta = n_e/\beta, \qquad (\partial p/\partial\beta)_\nu = -h/\beta \tag{97}$$

where h is the enthalpy per unit volume, lead to the relation between $\delta\nu$ and $\delta\beta$

$$\delta\nu = (h/n_e)\delta\beta \tag{98}$$

Consequently D becomes

$$\begin{aligned} D = \int_{-\infty}^{t} dt' \int dv\, \{&[\mathbf{s}(x,t',t) - (h/\rho)\mathbf{p}(x,t',t)] \cdot \nabla\beta(x,t') \\ &+ [u(x,t',t) - (h/n_e)n(x,t',t) + p]\partial\beta(x,t')/\partial t'\} \end{aligned} \tag{99}$$

One then obtains for the mean heat flux

$$s_i^\star(x,t) = \int_{-\infty}^{t} dt' \int dv' \left\{ \frac{\partial\beta(x',t')}{\partial x_j'} \langle s_i(x)[s_j(x',t',t) - (h/\rho)p_j(x',t',t)];t\rangle_L \right.$$
$$\left. + \frac{\partial\beta(x',t')}{\partial t'} \langle s_i(x)[u(x',t',t) - (h/n_e)n(x',t',t) + p];t\rangle_L \right\} \tag{100}$$

In the linear approximation the average over local equilibrium can be replaced by an equilibrium average, denoted by $\langle\ \rangle_0$, and hence

$$s_i^\star(x,t) = \int_{-\infty}^{t} dt' \int dv' \left\{ \frac{\partial\beta(x',t')}{\partial x_j'} \langle s_i(x)[s_j(x',t',t) - (h/\rho)p_j(x',t',t)]\rangle_0 \right.$$
$$\left. + \frac{\partial\beta(x',t')}{\partial t'} \langle s_i(x)[u(x',t',t) - (h/n_e)n(x',t',t) + p]\rangle_0 \right\} \tag{101}$$

According to the above formula the heat flux at a point x and time t depends on the temperature throughout the surrounding medium and at earlier times. Thus the transport relation is in general non-local. However, it is expected that, at least for the systems under consideration, the main contribution to the integral (101) will come from points x' which are near x, and times t' near t. This can be considered to be a consequence of molecular chaos: those molecules which contribute to the heat flux at x will remember their past history only throughout a small surrounding neighborhood. For a gas the dimensions of this neighborhood are of the order of the mean free path, and the significant time intervals are of the order of the mean time between collisions. Thus the non-locality covers only a limited region, and if the temperature gradient is sensibly constant over this region one expects the local Fourier law to hold.

The expression (101) also exhibits a dependence on the boundary forces, which affect the time dependence of the phase functions. However, for points far (many free paths) from a boundary it is expected that this dependence can be ignored. In fact, the transport relations should involve only properties of the medium, independently of the boundary conditions. Thus the time dependence in Eq. (101) can be determined by the equations of motion for an unbounded isolated medium, or

$$A(t',t) = A(t' - t) \tag{102}$$

where A denotes any of the phase functions appearing in Eq. (101), and the time dependence of $A(t)$ is governed by

$$\partial A(t)/\partial t = \{A(t),H\} \tag{103}$$

The boundary forces are to be neglected in Eq. (103), and hence the total particle number, energy, and momentum become constants of the motion.

We now follow the Chapman–Enskog procedure.[5] To lowest order the transport relations are those appropriate to local equilibrium. Since we have assumed the local velocity to vanish, the heat flux also vanishes in this approximation, and consequently the time derivative of the temperature vanishes. (Actually there is a contribution to the conservation law from the sources w, but this can be neglected at points far from a boundary.) Equation (101) then reduces to

$$s_i^\star(x,t) = \int_{-\infty}^{t} dt' \int dv' \, \frac{\partial \beta(x',t')}{\partial x_j'} \langle s_i(x)[s_j(x',t'-t) - (h/\rho)p_j(x,t'-t)]\rangle_0 \tag{104}$$

To the approximation under consideration the temperature gradient can be treated as constant. Actually however we wish to maintain the initial condition that the system is in equilibrium at $t = -\infty$, and consequently we put

$$\nabla\beta(x,t') = e^{\varepsilon(t'-t)}\nabla\beta(x,t) \tag{105}$$

The parameter ε is assumed to be small and positive, and the conditions under which the limit $\varepsilon \rightarrow 0$ can be taken will be discussed below.

The expression (104) for the heat flux now reduces to Fourier's law,

$$s_i^\star = -\lambda_{ij}\partial T/\partial x_j \tag{106}$$

where

$$\lambda_{ij} = (1/kT^2)\int_{-\infty}^{0} dt \, e^{\varepsilon t} \int dv' \, \langle s_i(x)[s_j(x',t) - (h/\rho)p_j(x',t)]\rangle_0 \tag{107}$$

is the thermal conductivity tensor. For a homogeneous system λ_{ij} is independent of x, so that

$$\lambda_{ij} = (1/\Omega k T^2) \int_{-\infty}^{0} dt\, e^{\epsilon t} \langle S_i [S_j(t) - \hat{S}_j] \rangle_0 \tag{108}$$

where

$$\mathbf{S} = \int dv\, \mathbf{s}(x) \tag{109}$$

and

$$\hat{\mathbf{S}} = h\mathbf{P}/\rho \tag{110}$$

$\hat{\mathbf{S}}$ is time-independent because of the constancy of the total momentum. Under conditions of spherical symmetry, as in a fluid, the conductivity tensor reduces to a scalar, and

$$\mathbf{s}^\star = -\lambda \nabla T \tag{111}$$

with

$$\lambda = (1/3\Omega k T^2) \int_{-\infty}^{0} dt\, e^{\epsilon t} \langle \mathbf{S} \cdot [\mathbf{S}(t) - \hat{\mathbf{S}}] \rangle_0 \tag{112}$$

This is Green's formula[9] for the thermal conductivity.

In the next approximation one obtains effects depending on the second derivatives of the temperature. There is no contribution to the heat flux in this approximation as a consequence of spherical symmetry, but one does obtain thermal stresses. Thus we consider the mean stress tensor

$$\begin{aligned} t^\star_{ij}(x,t) = \int_{-\infty}^{t} dt' \int dv' \Bigg\{ & \frac{\partial \beta(x',t')}{\partial x'_k} \langle t_{ij}(x)[s_k(x',t'-t) - (h/\rho) p_k(x',t'-t)] \rangle_0 \\ & + \frac{\partial \beta(x',t')}{\partial t'} \langle t_{ij}(x)[u(x',t'-t) - (h/n_e) n(x',t'-t) + p] \rangle_0 \Bigg\} \end{aligned} \tag{113}$$

The conservation law based on Eq. (111) is

$$\partial u_e / \partial t = \lambda \nabla^2 T \tag{114}$$

which gives for the time derivative of the temperature

$$\partial T / \partial t = (\lambda / c_p) \nabla^2 T \tag{115}$$

where c_p is the specific heat at constant pressure. Consider the second term of Eq. (113). In view of Eq. (115) this is already of second order in the temperature derivatives, and one may therefore ignore the space and time variation of $\nabla^2 T$. The result is then proportional to

$$\begin{aligned}\int dv' \, \langle t_{ij}(x)[u(x',t'-t) - (h/n_e)n(x',t'-t) + p]\rangle_0 \\ = \langle t_{ij}(x)[H - (h/n_e)N + p\Omega]\rangle_0 \qquad (116)\end{aligned}$$

Now denoting the averages of H and N by $\bar{H}$ and $\bar{N}$, we have

$$p\Omega = -\bar{H} + (h/n_e)\bar{N} \qquad (117)$$

and

$$\begin{aligned}\langle t_{ij}(x)[H - (h/n_e)N + p\Omega]\rangle_0 &= \langle t_{ij}(x)[H - \bar{H} - (h/n_e)(N - \bar{N})]\rangle_0 \\ &= \delta_{ij}[-(\partial p/\partial \beta)_v - (h/n_e)(\partial p/\partial v)_\beta] \\ &= 0 \qquad (118)\end{aligned}$$

Thus there is no contribution from the second term of Eq. (113).

Considering the first term, we make the expansion

$$\begin{aligned}\nabla\beta(x',t') = \nabla\beta(x,t) + (x_i' - x_i)\partial\nabla\beta(x,t)/\partial x_i \\ + (t'-t)\partial\nabla\beta(x,t)/\partial t + \cdots \qquad (119)\end{aligned}$$

The leading term gives no contribution to the stress tensor because of spherical symmetry. Furthermore, the third term is, as a consequence of Eq. (115), proportional to a third derivative and is therefore to be ignored. Thus, we are left with

$$\begin{aligned}t_{ij}^\star(x,t) = \frac{\partial^2\beta(x,t)}{\partial x_k \partial x_m} \int_{-\infty}^{0} dt \, e^{\epsilon t} \int dv'(x_m' - x_m) \\ \times \langle t_{ij}(x)[s_k(x',t) - (h/\rho)p_k(x',t)]\rangle_0 \qquad (120)\end{aligned}$$

Here we have again introduced a factor $e^{\epsilon t}$, rather than completely ignoring the time dependence of the temperature. Equation (120) may be further reduced to

$$t_{ij}^\star = -\zeta\partial^2 T/\partial x_i \partial x_j - \zeta'\delta_{ij}\nabla^2 T \qquad (121)$$

where

$$\begin{aligned}\zeta &= (1/15kT^2)\int_{-\infty}^{0} dt\, e^{\varepsilon t}\int dv'(x_j' - x_j)\\ &\qquad \times \langle[3t_{ij}(x) - \delta_{ij}t_{kk}(x)][s_i(x',t) - (h/\rho)p_i(x',t)]\rangle_0\\ \zeta' &= (1/15kT^2)\int_{-\infty}^{0} dt\, e^{\varepsilon t}\int dv'(x_j' - x_j) \qquad\qquad (122)\\ &\qquad \times \langle[2\delta_{ij}t_{kk}(x) - t_{ij}(x)][s_i(x',t) - (h/\rho)p_i(x',t)]\rangle_0\end{aligned}$$

We now consider the more general situation, with non-vanishing local velocity. In addition we suppose the system to contain more than one kind of particle in order to be able to treat diffusion. It is convenient to split D into two parts

$$D = D_1 + D_2 \qquad (123)$$

where

$$\begin{aligned}D_1 &= \int_{-\infty}^{t} dt' \int dv'\{\mathbf{s}(x',t',t)\cdot\nabla\beta(x',t') - \sum_k \mathbf{j}^k(x',t',t)\cdot\nabla\nu^k(x',t')\\ &\qquad - \beta\mathbf{p}(x',t',t)\cdot\partial\mathbf{v}(x',t')/\partial t'\}\\ D_2 &= \int_{-\infty}^{t} dt' \int dv'\{-\beta t_{ij}(x',t',t)\partial v_i(x',t')/\partial x_j' \qquad\qquad (124)\\ &\qquad + [u(x',t',t) - u_e]\partial\beta(x',t')/\partial t'\\ &\qquad - \sum_k [n^k(x',t',t) - n_e^k]\partial\nu^k(x',t')/\partial t'\}\end{aligned}$$

The purpose of this division is that, in the approximation to be considered, D_1 does not contribute to the mean stress tensor and D_2 does not contribute to the mean energy and particle fluxes.

In the lowest approximation the conservation laws become

$$\begin{aligned}\partial n_e^k/\partial t &= -n_e^k\nabla\cdot\mathbf{v}\\ \partial u_e/\partial t &= -h\nabla\cdot\mathbf{v} \qquad\qquad (125)\\ \partial\mathbf{v}/\partial t &= -\nabla p/\rho\end{aligned}$$

These are to be used to eliminate the time derivatives in D. Considering first D_1, we need the third of Eqs. (125). The identities

$$(\partial p/\partial\beta)_\nu = -h/\beta, \qquad (\partial p/\partial\nu^k)_\beta = n_e^k/\beta \qquad (126)$$

yield

$$\partial \mathbf{v}/\partial t = (h/\beta\rho)\nabla\beta - \sum_k (n_e^k/\beta\rho)\nabla\nu^k \tag{127}$$

and D_1 becomes

$$D_1 = \int_{-\infty}^{t} dt' \int dv' \, \{[\mathbf{s}(x',t',t) - (h/\rho)\mathbf{p}(x',t',t)] \cdot \nabla\beta(x',t') \\ - \sum_k [\mathbf{j}^k(x',t',t) - (n_e^k/\rho)\mathbf{p}(x',t',t)] \cdot \nabla\nu^k(x',t')\} \tag{128}$$

Following the earlier discussion, the space and time variation of temperature and chemical potential may be neglected, and one finds for the mean heat flux (assuming spherical symmetry)

$$\mathbf{s}^\star = -\lambda\nabla T - \sum_k L_k \nabla\nu^k \tag{129}$$

with λ given by the previous expression (112), and

$$L_k = (1/3\Omega)\int_{-\infty}^{0} dt \, e^{\varepsilon t}\langle \mathbf{S} \cdot [\mathbf{J}^k(t) - \hat{\mathbf{J}}^k]\rangle_0 \tag{130}$$

Here we have defined

$$\mathbf{J}^k = \int dv \, \mathbf{j}^k(x) \tag{131}$$

and

$$\hat{\mathbf{J}}^k = n_e^k \mathbf{P}/\rho \tag{132}$$

We note that

$$\sum_k m^k L_k = 0 \tag{133}$$

as a consequence of Eq. (36). In a similar way one obtains

$$\mathbf{j}^{\star k} = -L_k' \nabla T - \sum_{k'} L_{kk'} \nabla\nu^{k'} \tag{134}$$

with

$$L_k' = (1/3\Omega k T^2)\int_{-\infty}^{0} dt \, e^{\varepsilon t}\langle \mathbf{J}^k \cdot [\mathbf{S}(t) - \hat{\mathbf{S}}]\rangle_0 \tag{135}$$

$$L_{kk'} = (1/3\Omega)\int_{-\infty}^{0} dt \, e^{\varepsilon t}\langle \mathbf{J}^k \cdot [\mathbf{J}^{k'}(t) - \hat{\mathbf{J}}^{k'}]\rangle_0 \tag{136}$$

The coefficients L_k and L_k' describe the Soret and Dufour effects, while $L_{kk'}$ are the coefficients of diffusion. According to Onsager's theorem, these satisfy the relations

$$L_k = L'_k, \qquad L_{kk'} = L_{k'k} \tag{137}$$

as a consequence of time reversibility.

Consider next the mean stress tensor. It is convenient to utilize the condition that $\mathbf{v}$ be tangential to the boundary to alter the form of D_2 to

$$\begin{aligned} D_2 = \int_{-\infty}^{t} dt' \int dv' \, \{ & -\beta[t_{ij}(x',t',t) - p\delta_{ij}]\partial v_i(x',t')/\partial x'_j \\ & + [u(x',t',t) - u_e]\partial\beta(x',t')/\partial t' \\ & - \sum_k [n^k(x',t',t) - n^k_e]\partial \nu^k(x',t')/\partial t' \} \end{aligned} \tag{138}$$

with variations in the pressure p being neglected. It is now necessary to solve the first two of Eqs. (125) for $\partial\beta/\partial t$ and $\partial\nu^k/\partial t$, and then substitute into D_2. We have

$$\begin{aligned} \partial\beta/\partial t &= (\partial\beta/\partial u)_n(\partial u/\partial t) + \sum_k (\partial\beta/\partial n^k)_u(\partial n^k/\partial t) \\ &= [-h(\partial\beta/\partial u)_n - \sum_k n^k_e(\partial\beta/\partial n^k)_u]\nabla \cdot \mathbf{v} \\ &= -\beta\nabla \cdot \mathbf{v}[-(\partial p/\partial\beta)_\nu(\partial\beta/\partial u)_n + \sum_k (\partial p/\partial \nu^k)_\beta(\partial\beta/\partial n^k)_u] \end{aligned}$$

The identity

$$(\partial\beta/\partial n^k)_u = -(\partial\nu^k/\partial u)_n \tag{139}$$

enables one to write

$$\begin{aligned} \partial\beta/\partial t &= \beta\nabla \cdot \mathbf{v}[(\partial p/\partial\beta)_\nu(\partial\beta/\partial u)_n + \sum_k (\partial p/\partial\nu^k)_\beta(\partial\nu^k/\partial u)_n] \\ &= \beta\nabla \cdot \mathbf{v}(\partial p/\partial u)_n \end{aligned} \tag{140}$$

In a similar manner one finds

$$\partial\nu^k/\partial t = -\beta\nabla \cdot \mathbf{v}(\partial p/\partial n^k)_u \tag{141}$$

Thus D_2 becomes

$$\begin{aligned} D_2 = -\beta \int_{-\infty}^{t} dt' \int dv' \, & \partial v_i(x',t')/\partial x'_j \\ & \times \{t_{ij}(x',t',t) - \delta_{ij}[p + (\partial p/\partial u)_n(u(x',t',t) - u_e) \\ & + \sum_k (\partial p/\partial n^k)_u(n^k(x',t',t) - n^k_e)]\} \end{aligned} \tag{142}$$

The mean stress tensor is then found to be

$$t_{ij}^{\star}(x,t) = -\beta \partial v_k(x,t)/\partial x_m \int_{-\infty}^{0} dt\, e^{\epsilon t} \langle t_{ij}(x)[T_{km}(t) - \hat{T}_{km}]\rangle_0 \tag{143}$$

where

$$T_{ij} = \int dv\, t_{ij} \tag{144}$$

and we have introduced

$$\hat{T}_{ij} = \delta_{ij}[p\Omega + (\partial p/\partial u)_n(H - \bar{H}) + \sum_k (\partial p/\partial n^k)_u(N^k - \bar{N}^k)] \tag{145}$$

On taking account of spherical symmetry one can reduce Eq. (143) to

$$t_{ij}^{\star} = -\eta \left[\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3}\delta_{ij}\nabla \cdot \mathbf{v}\right] - \kappa \delta_{ij} \nabla \cdot \mathbf{v} \tag{146}$$

where the shear and bulk viscosities η and κ are given by

$$\begin{aligned} \eta &= (1/30\Omega kT) \int_{-\infty}^{0} dt\, e^{\epsilon t} \langle T_{ij}[3T_{ij}(t) - \delta_{ij} T_{kk}(t)]\rangle_0 \\ \kappa &= (1/9\Omega kT) \int_{-\infty}^{0} dt\, e^{\epsilon t} \langle T_{ii}[T_{kk}(t) - \hat{T}_{kk}]\rangle_0 \end{aligned} \tag{147}$$

For a low density monatomic gas, $p = \frac{2}{3}u$, and $\hat{T}_{ij}$ reduces to $\hat{T}_{ij} = \delta_{ij}\frac{2}{3}H$. Furthermore, with the intermolecular potential neglected, $T_{kk} = 2H$. Thus we see immediately from Eq. (147) that the bulk viscosity vanishes. However, with polyatomic molecules relaxation processes will give a non-vanishing bulk viscosity even at low densities.

The results (130), (135), (136), and (147) were also first obtained by Green.[9]

The extension of the transport relations to higher order is straightforward but algebraically complicated, and we will not continue in this direction. Instead, we consider certain general properties of the transport coefficients which have the form

$$L = \int_{-\infty}^{0} dt\, e^{\epsilon t} \langle F[G(t) - \hat{G}]\rangle_0 \tag{148}$$

where F and G denote any of $\mathbf{J}$, $\mathbf{S}$, and T_{ij}, and numerical factors have been neglected.

We first show that the cap in Eq. (148) is equivalent to a time average. Denote the time average by G_t. Then it must be a function only of constants of the motion, and we assume the only such constants are N, H, and $\mathbf{P}$:

$$G_t = G(N,H,\mathbf{P}) \tag{149}$$

Expanding about the average values $\bar{N}$, $\bar{H}$, and $\bar{\mathbf{P}} = 0$, we find

$$\begin{aligned} G_t = G(\bar{N},\bar{H},\bar{\mathbf{P}}) &+ (N - \bar{N})\partial G(\bar{N},\bar{H},\bar{\mathbf{P}})/\partial\bar{N} \\ &+ (H - \bar{H})\partial G(\bar{N},\bar{H},\bar{\mathbf{P}})/\partial\bar{H} \\ &+ (\mathbf{P} - \bar{\mathbf{P}})\partial G(\bar{N},\bar{H},\bar{\mathbf{P}})/\partial\bar{\mathbf{P}} + \cdots \end{aligned} \tag{150}$$

In a grand canonical ensemble the fluctuations in N, H, and $\mathbf{P}$ are small, and succeeding terms in the above expansion will give contributions which are negligible for a large system. Now suppose $G = \mathbf{S}$. Then $\mathbf{S}$, as well as its derivatives with respect to $\bar{N}$ and $\bar{H}$, must vanish in equilibrium from symmetry. Hence $\mathbf{S}_t$ has the form

$$\mathbf{S}_t = a(\mathbf{P} - \bar{\mathbf{P}}) = a\mathbf{P} \tag{151}$$

where a is a function only of $\bar{N}$ and $\bar{H}$. To evaluate a, consider

$$\langle \mathbf{P} \cdot \mathbf{S}_t \rangle_0 = \langle \mathbf{P} \cdot \mathbf{S} \rangle_0 = a\langle P^2 \rangle_0 \tag{152}$$

The average over equilibrium can be broken down into an average over the manifold of states with a given momentum $\mathbf{P}$, denoted by $\langle\ \rangle_{\mathbf{P}}$, followed by an average over the values of $\mathbf{P}$. Thus

$$\langle \mathbf{P} \cdot \mathbf{S} \rangle_0 = \langle \mathbf{P} \cdot \langle \mathbf{S} \rangle_{\mathbf{P}} \rangle_0 \tag{153}$$

But $\langle \mathbf{S} \rangle_{\mathbf{P}}$ is the mean energy flux, integrated over the volume, for a system in equilibrium and moving with the velocity $\mathbf{v} = \mathbf{P}/M$, where M is the total mass. Consequently we have

$$\langle \mathbf{S} \rangle_{\mathbf{P}} = (\bar{H} + p\Omega)\mathbf{P}/M \tag{154}$$

and

$$\langle \mathbf{P} \cdot \langle \mathbf{S} \rangle_{\mathbf{P}} \rangle_0 = (\bar{H} + p\Omega)\langle P^2/M \rangle_0 \tag{155}$$

giving for a

$$a = (\bar{H} + p\Omega)/M = h/\rho \tag{156}$$

$\mathbf{S}_t$ is then seen to be identical with $\hat{\mathbf{S}}$ as defined by Eq. (110). In a similar manner one finds

$$\mathbf{J}_t^k = n_e^k \mathbf{P}/\rho \tag{157}$$

which with Eq. (132) shows the identity of $\mathbf{J}_t^k$ and $\hat{\mathbf{J}}^k$. Finally, the expression (145) for $\hat{T}_{ij}$ is precisely the expansion (150). Thus in all cases the Green formulae involve the difference between a flux and its time average.

The expression

$$\langle \hat{F}[G(t) - \hat{G}] \rangle_0 \tag{158}$$

is clearly time-independent, and must therefore be equal to its time average:

$$\langle \hat{F}[G(t) - \hat{G}] \rangle_0 = \langle \hat{F}[\hat{G} - \hat{G}] \rangle_0 = 0 \tag{159}$$

Consequently, one may write Eq. (148) in the symmetric form

$$L = \int_{-\infty}^{0} dt\, e^{\varepsilon t} \langle [F - \hat{F}][G(t) - \hat{G}] \rangle_0 \tag{160}$$

According to the second law of thermodynamics the transport coefficients for $F = G$ (that is, the thermal conductivity, shear and bulk viscosities, and coefficients of diffusion) cannot be negative. To show that this is actually the case, consider the inequality

$$I \equiv \left\langle \left\{ \int_{-\infty}^{0} dt\, e^{\varepsilon t} [G(t) - \hat{G}] \right\}^2 \right\rangle_0 \geqslant 0 \tag{161}$$

Clearly we have

$$I = \int_{-\infty}^{0} dt\, e^{\varepsilon t} \int_{-\infty}^{0} dt'\, e^{\varepsilon t'} \langle [G(t) - \hat{G}][G(t') - \hat{G}] \rangle_0 \tag{162}$$

For an isolated system the above correlation function depends only on the difference $t' - t$ and a change of variables then yields

$$\begin{aligned} I &= \int_{-\infty}^{0} dt\, e^{\varepsilon t} \int_{-\infty}^{0} dt'\, e^{\varepsilon t'} \langle [G - \hat{G}][G(t' - t) - \hat{G}] \rangle_0 \\ &= \int_{-\infty}^{0} dt\, e^{2\varepsilon t} \int_{-\infty}^{-t} d\tau\, e^{\varepsilon t} \langle [G - \hat{G}][G(\tau) - \hat{G}] \rangle_0 \end{aligned} \tag{163}$$

On integrating by parts we find

$$I = (1/\varepsilon) \int_{-\infty}^{0} dt\, e^{\varepsilon t} \langle [G - \hat{G}][G(t) - \hat{G}] \rangle_0 \tag{164}$$

which yields the desired result,

$$L = \varepsilon I \geqslant 0 \tag{165}$$

Consider next the behavior of L for $\varepsilon \to 0$. For simplicity we will take $F = G$, although the following remarks apply equally well if $F \neq G$. If the limit $\varepsilon \to 0$ is to exist, it is clearly necessary that

$$\lim_{\varepsilon \to 0} \varepsilon \int_{-\infty}^{0} dt\, e^{\varepsilon t} \langle [G - \hat{G}][G(t) - \hat{G}] \rangle_0 = 0 \tag{166}$$

This in turn requires that the time average vanish,

$$\lim_{T \to \infty} \frac{1}{T} \int_{-T}^{0} dt\, \langle [G - \hat{G}][G(t) - \hat{G}] \rangle_0 = 0 \tag{167}$$

That the above time average does indeed vanish is an immediate consequence of the fact that $\hat{G}$ is the time average of G; this in turn can be traced to the determination of the thermodynamic variables according to Eq. (69). (Refer back to Eq. (125) and the subsequent discussion, where the definition of thermodynamic variables has been utilized in eliminating the time derivatives from D.)

In the above derivation there is a certain ambiguity at some points, for example, in introducing the pressure p into Eq. (138). This ambiguity is to be settled by the requirement that the limit (167) vanish, that is, that $\hat{G}$ actually be the time average of G; otherwise one clearly does not obtain a legitimate approximation to the transport relation. An additional ambiguity concerns the definition of the fluxes since, as already remarked, one can add to them any quantity with vanishing divergence. We have already introduced certain restrictions as in Eq. (41), and it appears, although we have not been able to prove it, that any remaining arbitrariness can also be settled by Eq. (167).

The preceding remarks have a close analog in the Chapman–Enskog[5] theory. There at some points one encounters an element of ambiguity due to the possibility of adding linear combinations of the collisional invariants. This ambiguity is removed by requiring that certain integral equations have solutions, which in turn is necessary for the consistency of the method. The existence of solutions to these equations is closely connected to the condition (167).

To proceed further it is convenient to use the formalism of quantum mechanics. As will be seen in Section XI one then obtains for the transport coefficients formulae which are similar to (160), but because of non-commutation of the operators F and $G(t)$ it is necessary to take the real part,

$$L = \operatorname{Re} \int_{-\infty}^{0} dt\, e^{\varepsilon t} \langle G[G(t) - \hat{G}] \rangle_0 \tag{168}$$

We expand the correlation function in terms of the energy eigenvectors ψ_i,

$$H\psi_i = E_i \psi_i \tag{169}$$

with the result

$$\langle G[G(t) - \hat{G}] \rangle_0 = \sum_{i,j} f_0(E_i) G_{ij} (G - \hat{G})_{ji} e^{i\omega_{ji} t} \tag{170}$$

where G_{ij} denotes the matrix elements of G with respect to the ψ_i, f_0 is the equilibrium density matrix, and $\omega_{ij} = (E_i - E_j)/\hbar$. Now the time average

$$\lim_{T\to\infty} \frac{1}{T} \int_{-T}^{0} dt\, e^{i\omega_{ji} t} \tag{171}$$

vanishes unless $\omega_{ji} = 0$, in which case it is equal to 1. Thus the subtraction of the time average $\hat{G}$ in (170) has the effect of eliminating those terms in the double sum for which $\omega_{ji} = 0$, and hence

$$\begin{aligned} L &= \operatorname{Re} \sum_{\omega_{ji} \neq 0} f_0(E_i) |G_{ij}|^2 \int_{-\infty}^{0} dt\, e^{\varepsilon t}\, e^{i\omega_{ji} t} \\ &= \sum_{\omega_{ji} \neq 0} f_0(E_i) |G_{ij}|^2 \frac{\varepsilon}{\omega_{ji}^2 + \varepsilon^2} \end{aligned} \tag{172}$$

Now since terms with $\omega_{ji} = 0$ do not appear, the limit vanishes,

$$\lim_{\varepsilon \to 0} L = 0 \tag{173}$$

This difficulty occurs because we have considered a finite system; the correlation function (170) is then an almost periodic function, with recurrence properties. Evidently the flux G takes on positive and negative values equally, and cancellations then give a vanishing result for $\varepsilon \to 0$. If one first takes the limit of an infinite system then, as we shall see, a non-vanishing result is obtained for $\varepsilon \to 0$. However this does not mean that the transport coefficients are undefined for a finite system; rather they exhibit a dependence on the past history of the system which cannot be entirely eliminated. Certainly if $1/\varepsilon$ is chosen to be of the order of, say, one hour the dependence of L on ε is extremely weak.

For infinite volume denote the eigenvectors, which now form a continuous set, by $|E\rangle$. (For simplicity we will not explicitly indicate those variables in addition to the energy which are necessary to completely specify the state. In the following where integrals over energy appear they should be understood to include a sum or integration over the extra variables.) We separate the matrix elements of G, denoted by $\langle E|G|E'\rangle$, into diagonal and non-diagonal parts according to

$$\langle E|G|E'\rangle = G(E)\delta(E - E') + \langle E|G'|E'\rangle \tag{174}$$

the separation being determined by the requirement that the last term be finite for $E = E'$ (or at least not contain a factor $\delta(E - E')$). The time dependence is given by

$$\langle E|G(t)|E'\rangle = G(E)\delta(E - E') + \langle E|G'|E'\rangle \exp i(E - E')t/\hbar \tag{175}$$

On taking the time average the second term vanishes except at $E = E'$, where it is finite. In subsequent integrations the contribution from this single point is negligible, and hence

$$\langle E|\hat{G}|E'\rangle = G(E)\delta(E - E') \tag{176}$$

Consequently we obtain

$$\begin{aligned} \langle E|(G - \hat{G})|E'\rangle &= \langle E|G'|E'\rangle \\ \langle E|(G(t) - \hat{G})|E'\rangle &= \langle E|G'|E'\rangle \exp i(E - E')t/\hbar \end{aligned} \tag{177}$$

Equation (168) then takes on the form

$$L = \int dE \int dE' f_0(E) |\langle E|G'|E'\rangle|^2 \frac{\varepsilon}{\varepsilon^2 + (E - E')^2/\hbar^2} \tag{178}$$

The limit $\varepsilon \to 0$ can now be taken, and yields a non-vanishing result,

$$L = \pi\hbar \int dE \int dE' f_0(E) |\langle E|G'|E'\rangle|^2 \delta(E - E') \tag{179}$$

It should be noted that the correlation function $\langle G(G(t) - \hat{G})\rangle_0$, and consequently L, is evidently an extensive quantity, that is, is proportional to Ω. However, this dependence is cancelled by the factor $1/\Omega$ appearing in the Green formulae.

X. IONIZED MEDIUM

As remarked in Section VI the treatment of local equilibrium must be modified for charged particles, since the long-range coulomb interaction induces long-range correlations and neighboring volume elements cannot be considered to be statistically independent. We will indicate how the coulomb interaction can be taken into account by means of a self-consistent field, as in the Debye–Hückel theory.[15] The results are then valid under the same conditions as the Debye–Hückel theory, namely when the Debye radius is large compared to the mean interparticle separation.

The potential for the self-consistent field is determined by

$$\nabla^2\varphi(x,t) = -4\pi \sum_k e^k \langle n^k(x);t\rangle_L \tag{180}$$

where e^k is the charge per particle of species k. The effect of the coulomb interaction can be taken into account by altering the chemical potentials according to

$$\mu^k \to \mu^k - e^k\beta\varphi \tag{181}$$

The mean particle density, averaged over local equilibrium, is then

$$\langle n^k(x);t\rangle_L = n_e^k[\beta(x,t),\nu^k(x,t) - e^k\beta(x,t)\varphi(x,t)] \tag{182}$$

where n_e^k is again the same function of its arguments as in equilibrium.

It is necessary to maintain the conditions (69) in order that the limit (167) will vanish. Consequently, in view of Eq. (182) the mean particle densities do not depend on $\nu^k(x,t)$ in the same way as in equilibrium, and $\mu^k(x,t) = \nu^k(x,t)/\beta(x,t)$ cannot be interpreted as the chemical potentials. Instead we introduce

$$\bar{\mu}^k(x,t) = \mu^k(x,t) - e^k\varphi(x,t), \qquad \bar{\nu}^k(x,t) = \beta(x,t)\bar{\mu}^k(x,t) \tag{183}$$

and treat the $\bar{\mu}^k$ as the chemical potentials, since they give the proper values of the mean particle densities.

In the transport relations ν^k is to be replaced by its value as given by Eq. (183),

$$\nu^k(x,t) = \bar{\nu}^k(x,t) + e^k\beta(x,t)\varphi(x,t) \tag{184}$$

This is of course a consequence of the well-known thermodynamic result that the chemical and electric potentials occur only in the combination $\bar{\mu}^k + e^k\varphi$. For linear processes $\beta(x,t)$ is to be treated as constant in Eq. (184), and the transport relation (134) becomes

$$\mathbf{j}^{\star k} = -L'_k\nabla T - \sum_{k'} L_{kk'}\nabla\bar{\nu}^{k'} - \beta\sum_{k'} L_{kk'}e^{k'}\nabla\varphi \tag{185}$$

The electric current density $\boldsymbol{i}$ is obtained immediately as

$$\begin{aligned} \boldsymbol{i} &= \sum_k e^k\mathbf{j}^{\star k} \\ &= -\sum_k e^k L'_k\nabla T - \sum_{k,k'} e^k L_{kk'}\nabla\bar{\nu}^{k'} - \beta\sum_{k,k'} e^k e^{k'} L_{kk'}\nabla\varphi \end{aligned} \tag{186}$$

which identifies the electrical conductivity σ as

$$\sigma = \beta\sum_{k,k'} e^k e^{k'} L_{kk'} \tag{187}$$

For a system with overall electrical neutrality one finds from Eq. (132)

$$\sum_k e^k\hat{\mathbf{J}}^k = \sum_k e^k n_e^k\mathbf{P}/\rho = 0 \tag{188}$$

and Eq. (136) for $L_{kk'}$ then yields

$$\sigma = (1/3\Omega kT)\int_{-\infty}^{0} dt\, e^{\epsilon t}\langle\mathbf{I}\cdot\mathbf{I}(t)\rangle_0 \tag{189}$$

where

$$\mathbf{I} = \sum_k e^k\mathbf{J}^k \tag{190}$$

The result (189) is Kubo's formula[13] for the electrical conductivity.

Equation (129) for the heat flux becomes

$$\mathbf{s}^\star = -\lambda \nabla T - \sum_k L_k \nabla \bar{\nu}^k - \beta \sum_k e^k L_k \nabla \varphi \tag{191}$$

The last term above and the first term of Eq. (186) describe the thermoelectric effects.

XI. QUANTUM THEORY

We next consider the extent to which the previous discussion must be modified to take into account the effects of quantum theory.

Hydrodynamics is basically a classical theory and consequently the effects of the uncertainty principle can be neglected for the hydrodynamic variables. To see this in detail we suppose the variation in the thermodynamic variables, temperature, chemical potential, and velocity, to be characterized by a length l; over distances of the order l these variables change by small amounts. One may then divide the system into volume elements with linear dimensions of the order a, and if $a < l$ the microscopic variables at a point may be replaced by their averages over the corresponding volume element. Now a particle can be localized to a region with dimensions of the order $\lambda = \hbar/\bar{p}$, where for $\bar{p}$ we may take the mean momentum per particle, or

$$\bar{p} \sim \sqrt{mkT} \tag{192}$$

with m being the mass per particle. If $\lambda < a$ then a particle can be localized to a single volume element and the wave functions for particles in different volume elements will not overlap. The microscopic variables referring to different volume elements may then be assumed to commute. Thus if the condition

$$l \gg \hbar/\bar{p} \tag{193}$$

or

$$l \gg \hbar/\sqrt{mkT} \tag{194}$$

is satisfied fluctuations of a quantum mechanical nature are small and the hydrodynamic variables are essentially classical. This condition is actually well satisfied for the processes of interest in hydrodynamics.

We note that for a degenerate electron gas the relation (192) is to be replaced by $\bar{p} \sim \sqrt{m\varepsilon_F}$, where ε_F is the Fermi energy, and hence Eq. (194) becomes

$$l \gg \hbar/\sqrt{m\varepsilon_F} \tag{195}$$

The condition (194) can be expressed in a different form as follows. Let the time dependence of the thermodynamic variables be characterized by a frequency ω. Then ω is related to l by $\omega \sim c/l$, where c has the order of the sound speed, or $c \sim \bar{p}/m$. We then find from Eq. (194)

$$\hbar\omega \ll kT \tag{196}$$

or, for an electron gas,

$$\hbar\omega \ll \varepsilon_F \tag{197}$$

If Eq. (196) is satisfied the equilibrium density matrix may be assumed to commute with the microscopic variables. In fact, letting A denote any of the latter, we have

$$[e^{-\beta H},A] \sim -\beta e^{-\beta H}[H,A] = \beta e^{-\beta H} i\hbar\dot{A} \tag{198}$$

where the brackets denote the commutator. But for $\dot{A}$ we may put approximately ωA, and hence

$$[e^{-\beta H},A] \sim i\hbar\omega\beta e^{-\beta H} A \tag{199}$$

which is small, as a consequence of Eq. (196). On the other hand, one may not neglect the commutator of H with the microscopic variables, since this would amount to ignoring their time dependence. Thus we may assume any two variables to commute, except when one of them is the hamiltonian.

With the above remarks in mind we consider the non-equilibrium ensemble in quantum mechanics. The ensemble for the universe is described by a density matrix ρ, satisfying the von Neumann equation

$$\frac{\partial \rho}{\partial t} + \frac{1}{i\hbar}[\rho,H_u] = 0 \tag{200}$$

We suppose the hamiltonian for the universe H_u to be separated as in Eq. (3) into a part referring to the system, one referring to the surroundings, plus an interaction.

Let q' and Q' be the eigenvalues of a complete set of commuting variables referring to the system and surroundings respectively. The density matrix f for the system is obtained from ρ by taking a trace over the variables Q',

$$\langle q'|f|q''\rangle = \sum_{Q'}\langle q',Q'|\rho|q'',Q'\rangle \tag{201}$$

or

$$f = \mathrm{Ts}\,\rho \tag{202}$$

where the operation Ts is defined by

$$\langle q'|\mathrm{Ts}\,A|q''\rangle = \sum_{Q'}\langle q',Q'|A|q'',Q'\rangle \tag{203}$$

for arbitrary A. Equation (200) then leads to the equation for f

$$\frac{\partial f}{\partial t} + \frac{1}{i\hbar}[f,H] + \frac{1}{i\hbar}\mathrm{Ts}[\rho,V] = 0 \tag{204}$$

The last term of Eq. (204) describes the interaction of the system with its surroundings, and as in Section III our problem is to characterize this interaction thermodynamically in terms of the temperature, chemical potential, and velocity associated with the surroundings. The procedure is similar to that followed earlier. Put

$$\rho = f\textstyle\prod_r g_r X_r \tag{205}$$

In accordance with the previous remarks we may suppose f, g_r, and X_r to commute with one another, but not with V for the same reason that commutators with the hamiltonian cannot be ignored. However, in view of the kinematical independence of different reservoirs we assume that $g_r X_r$ commutes with $V_{r'}$ for $r \neq r'$. Equation (204) then becomes

$$\frac{\partial f}{\partial t} + \frac{1}{i\hbar}[f,H] + \frac{1}{i\hbar}\sum_r \mathrm{Ts}[fg_rX_r,V_r] = 0 \tag{206}$$

Putting $f = e^{\eta}$, and again ignoring all commutators except with H or V, we find

$$\frac{\partial \eta}{\partial t} + \frac{1}{i\hbar}[\eta,H] + \frac{1}{i\hbar}\sum_r \mathrm{Ts}\{g_rX_r[\eta,V_r] + [g_rX_r,V_r]\} = 0 \tag{207}$$

Let A be an arbitrary time-independent operator, referring to the system alone. Denoting a trace over the system variables q' by Tr, we find from Eq. (206)

$$\begin{aligned}\frac{d}{dt}\operatorname{Tr} fA &= \operatorname{Tr}\frac{\partial f}{\partial t}A \\ &= \frac{1}{i\hbar}\operatorname{Tr} f\{[A,H] + \sum_r \operatorname{Ts} g_r X_r[A,V_r]\} \qquad (208)\end{aligned}$$

which identifies the Heisenberg equation of motion for the operator A as

$$\frac{dA}{dt} = \frac{1}{i\hbar}[A,H] + \frac{1}{i\hbar}\sum_r \operatorname{Ts} g_r X_r[A,V_r] \qquad (209)$$

Equation (207) can then be written as

$$\frac{d\eta}{dt} = -\frac{1}{i\hbar}\sum_r \operatorname{Ts}[g_r X_r, V_r] \qquad (210)$$

This result is to be compared with Eq. (15). Following the earlier procedure we evaluate the right-hand side by requiring that with a single reservoir present, Eq. (210) admit as a solution the equilibrium ensemble corresponding to a system with temperature T_r, chemical potential μ_r, and velocity $\mathbf{v}_r$. The right-hand side is then found to be given by the corresponding member of Eq. (30), with a minus sign.

The remainder of the discussion now follows the classical argument, with one slight exception. The operator η as determined from Eq. (210), and consequently $f = e^\eta$, is hermitian. If, however, we factor f as previously,

$$f = f_L e^D \qquad (211)$$

the result is not hermitian, owing to non-commutation of D and f_L. The non-hermitian part must be negligibly small, in view of our earlier remarks, but it is desirable to use an ensemble which is exactly hermitian. For this purpose we simply take the hermitian part of (211),

$$f = \tfrac{1}{2}[f_L e^D + e^D f_L] \qquad (212)$$

For linear processes we expand, $e^D = 1 + D + \cdots$, and the transport relations are obtained by following the earlier argument.

The transport coefficients have the same form as before, except that one takes the real part, that is, Eq. (148) becomes

$$L = \mathrm{Re} \int_{-\infty}^{0} dt\, e^{\epsilon t} \langle F[G(t) - \hat{G}] \rangle_0 \tag{213}$$

One can of course expand f in powers of D exactly, taking into account the non-commutation of the various operators. However, to the extent that the non-hermitian part of (211) is appreciable the basis of our discussion is invalid, and one may therefore just as well adopt the simpler procedure (212).

The quantum mechanical formula for electrical conductivity obtained by Kubo[13] is

$$\sigma = (1/3\Omega) \int_{0}^{\beta} d\lambda \int_{-\infty}^{0} dt\, e^{\epsilon t} \langle \mathbf{I} \cdot \mathbf{I}(t + i\hbar\lambda) \rangle_0 \tag{214}$$

Similar expressions, containing the extra integral over temperature, have been obtained by Mori[20] and by Kubo, Yokota, and Nakajima[14] for the other transport coefficients. It can be shown[24] that these expressions reduce to the form (213). However, it may appear that the procedure followed by these authors is less arbitrary than that adopted here, and may even be applicable when the condition (194) is not satisfied. That this is not the case, excepting for the moment electrical conduction, can be seen as follows. Mori and Kubo, Yokota, and Nakajima introduce thermodynamic variables by means of a local equilibrium distribution function. They then ignore correlations between neighboring volume elements, which amounts to assuming the condition (194). On the other hand if (194) is not satisfied the concept of local equilibrium is to a considerable extent arbitrary; one may express f_L in many different forms which are all equivalent classically, and these different forms will lead to different expressions for the transport coefficients.

We emphasize that the condition (194) is extremely weak. In fact if one assumes l to be as small as one micron, it is violated only for temperatures of the order 10^{-5} °K. Under such conditions it is doubtful if hydrodynamics is applicable, and in any event a more detailed analysis than that given here, or elsewhere, is necessary.

The case of electrical conduction is somewhat more straightforward. In Kubo's analysis an external electric field is introduced and the resulting electric current calculated by perturbation theory; the result (214) follows without the necessity of introducing the restriction (194). Thus Kubo's formula appears to be valid even when quantum fluctuations are large, although then one may question whether the use of a statistical ensemble is legitimate.

XII. DISCUSSION

We have at several points noted similarities to the Chapman–Enskog method in kinetic theory. This resemblance actually extends quite deep, and in order to demonstrate it in detail we obtain the normal solution to the Boltzmann equation in a form which will facilitate comparisons. For simplicity we consider linear processes only and therefore write the Boltzmann distribution function $f_B(\mathbf{q},\mathbf{c},t)$ as

$$f_B = f_0\,(1+\phi) \tag{215}$$

where

$$f_0 = n(\beta m/2\pi)^{3/2}\exp(-\tfrac{1}{2}\beta mc^2) \tag{216}$$

is the equilibrium Maxwell–Boltzmann distribution and ϕ is assumed to be small. Here and in the following paragraphs n denotes the mean number density and $\mathbf{q},\mathbf{c}$ the position and velocity of a molecule. The Boltzmann equation becomes

$$\partial\phi/\partial t + \mathbf{c}\cdot\nabla\phi + I'[\phi] = 0 \tag{217}$$

where I' is a linearized collision operator whose detailed form is unimportant for our purposes. (I' is equal to n^2/f_0 times the I of Chapman and Cowling.[5])

A state of local equilibrium is described by the distribution function

$$f_L = n(\mathbf{q},t)[\beta(\mathbf{q},t)m/2\pi]^{3/2}\exp\{-\tfrac{1}{2}\beta(\mathbf{q},t)m[\mathbf{c}-\mathbf{v}(\mathbf{q},t)]^2\} \tag{218}$$

where $T(\mathbf{q},t) = 1/k\beta(\mathbf{q},t)$, $n(\mathbf{q},t)$, and $\mathbf{v}(\mathbf{q},t)$ are the local temperature, mean density, and mean velocity at point $\mathbf{q}$ and time t. For states near equilibrium we expand to obtain

$$f_L = f_0\{1 - \delta\beta[\tfrac{1}{2}mc^2 - \tfrac{3}{2}kT] + \delta n/n + \beta m\mathbf{c}\cdot\mathbf{v}\} \tag{219}$$

where $\delta\beta = \beta(\mathbf{q},t) - \beta$, $\delta n = n(\mathbf{q},t) - n$, and $\mathbf{v} = \mathbf{v}(\mathbf{q},t)$ are assumed to be small. We now write

$$\phi = -\,\delta\beta[\tfrac{1}{2}mc^2 - \tfrac{3}{2}kT] + \delta n/n + \beta m\mathbf{c}\cdot\mathbf{v} + D \tag{220}$$

and determine D by the requirement that ϕ be a solution to the Boltzmann equation (217). Taking into account that 1, $\mathbf{c}$, and c^2 are summational invariants,

$$I'[1] = 0,\quad I'[\mathbf{c}] = 0,\quad I'[c^2] = 0 \tag{221}$$

one finds

$$\begin{aligned}\partial D/\partial t + \mathbf{c}\cdot\nabla D + I'[D] = [\tfrac{1}{2}mc^2 - \tfrac{3}{2}kT][\mathbf{c}\cdot\nabla\delta\beta + \partial\delta\beta/\partial t]\\ - (1/n)[\mathbf{c}\cdot\nabla\delta n + \partial\delta n/\partial t]\\ - \beta mc_ic_j\partial v_i/\partial q_j - \beta m\mathbf{c}\cdot\partial\mathbf{v}/\partial t\end{aligned} \tag{222}$$

As is easily verified by substitution a solution to the above equation is

$$\begin{aligned}D = \int_{-\infty}^{t} dt'\, e^{(t'-t)(I'+\mathbf{c}\cdot\nabla)}\{[\tfrac{1}{2}mc^2 - \tfrac{3}{2}kT][\mathbf{c}\cdot\nabla\delta\beta(\mathbf{q},t') + \partial\delta\beta(\mathbf{q},t')/\partial t']\\ - (1/n)[\mathbf{c}\cdot\nabla\delta n(\mathbf{q},t') + \partial\delta n(\mathbf{q},t')/\partial t']\\ - \beta mc_ic_j\partial v_i(\mathbf{q},t')/\partial q_j - \beta m\mathbf{c}\cdot\partial\mathbf{v}(\mathbf{q},t')/\partial t'\}\end{aligned} \tag{223}$$

This, in combination with Eqs. (215) and (220), constitutes the desired normal solution.

The Chapman–Enskog method may be applied directly to Eq. (223) to obtain f_B as an expansion in powers of the operator ∇, and in this manner one can verify that the solution obtained is in fact the usual normal solution, in the linear approximation. On the other hand, the closed form (223) may be useful for rapidly varying processes to which the Chapman–Enskog expansion is not applicable.

Equation (223) already bears a resemblance to our earlier result (54) [or rather to the linearized form of (54)]. To make the resemblance even closer we introduce the abbreviations

$$\begin{aligned}&n'(\mathbf{x}) = \delta(\mathbf{x}-\mathbf{q}),\ \mathbf{j}'(\mathbf{x}) = n'(\mathbf{x})\mathbf{c},\\ &u'(\mathbf{x}) = \delta(\mathbf{x}-\mathbf{q})[\tfrac{1}{2}mc^2 - \tfrac{3}{2}kT],\ \mathbf{s}'(\mathbf{x}) = u'(\mathbf{x})c,\\ &\mathbf{p}'(\mathbf{x}) = \delta(\mathbf{x}-\mathbf{q})m\mathbf{c},\ t'_{ij}(\mathbf{x}) = p_i(\mathbf{x})c_j = t'_{ji}(\mathbf{x}).\end{aligned} \tag{224}$$

For simplicity we will not explicitly indicate the dependence on $\mathbf{q}$, $\mathbf{c}$. In addition we define time-dependent quantities by

$$n'(\mathbf{x},t) = e^{t(I' + \mathbf{c}\cdot\nabla)} n'(\mathbf{x}) \tag{225}$$

with similar definitions for the other variables of (224). (Here the operator ∇ operates on $\mathbf{q}$ rather than on $\mathbf{x}$, and I' of course operates on functions of $\mathbf{c}$.) Equation (223) can then be written in the form

$$\begin{aligned} D = \int_{-\infty}^{t} dt' \int dv \{ & \mathbf{s}'(\mathbf{x},t'-t) \cdot \nabla\delta\beta(\mathbf{x},t') + u'(\mathbf{x},t'-t)\partial\delta\beta(\mathbf{x},t')/\partial t' \\ & - (1/n)[\mathbf{j}(\mathbf{x},t'-t) \cdot \nabla\delta n(x,t') + n'(\mathbf{x},t'-t)\partial\delta n(\mathbf{x},t')/\partial t'] \\ & - \beta t'_{ij}(\mathbf{x},t'-t)\partial v_i(\mathbf{x},t')/\partial x_j - \beta\mathbf{p}'(\mathbf{x},t'-t) \cdot \partial\mathbf{v}(\mathbf{x},t')/\partial t' \} \end{aligned} \tag{226}$$

where the inner integration extends over a region including the point $\mathbf{x} = \mathbf{q}$. Equation (226) is to be compared with (54). (Certain differences occur because in the earlier discussion the chemical potential rather than the density has been used as an independent variable.)

It is clear from its derivation that the ensemble (51) corresponds to a boundary-value problem. The same is true for the normal solution to the Boltzmann equation. This does not seem to be generally recognized but is easily shown. Perform an integration by parts on the second, fourth, and last terms of Eq. (226), assuming $\delta\beta$, δn, and $\mathbf{v}$ to vanish in the infinite past. On taking into account the conservation laws

$$\partial n'/\partial t + \nabla \cdot \mathbf{j}' = 0,\ \partial u'/\partial t + \nabla \cdot \mathbf{s}' = 0,\ \partial p'_i/\partial t + \partial t'_{ij}/\partial x_j = 0 \tag{227}$$

one finds

$$\begin{aligned} D = & \int dv[\delta\beta(\mathbf{x},t)u'(\mathbf{x}) - \delta n(\mathbf{x},t)n'(\mathbf{x})/n - \beta\mathbf{v}(\mathbf{x},t) \cdot \mathbf{p}(\mathbf{x})] \\ & + \int_{-\infty}^{t} dt' \int dA_i[\delta\beta(\mathbf{x},t')s'_i(\mathbf{x},t'-t) - \delta n(\mathbf{x},t')j'_i(\mathbf{x},t'-t)/n \\ & - \beta v_j(\mathbf{x},t')t'_{ij}(\mathbf{x},t'-t)] \end{aligned} \tag{228}$$

where dA_i is an element of area on the bounding surface. The distribution function f_B can then be reduced to

$$f_B = f_0 \Big\{1 + \int_{-\infty}^{t} dt' \int dA_i [\delta\beta(\mathbf{x},t') s_i'(\mathbf{x},t' - t) \\ - \delta n(\mathbf{x},t') j_i'(\mathbf{x},t' - t)/n - \beta v_j(\mathbf{x},t') t_{ij}'(\mathbf{x},t' - t)]\Big\} \tag{229}$$

From this result it is clear that the normal solution is specified by the past history of the boundary values of the temperature, mean density, and mean velocity of the gas.

The Chapman–Enskog approximation method leads, at all stages, to hydrodynamic equations which are first order in the time and can therefore be solved subject to given initial conditions. This procedure by which the boundary-value problem is converted into an initial-value problem is, from the mathematical point of view, somewhat mysterious. It appears likely that the procedure will converge only for processes whose scale of variation is of the order of, or less than, the mean free path (or other characteristic length). The reduction to an initial-value problem would then be impossible for rapidly varying processes.

We have repeatedly used the term hydrodynamic, and we now give it a more precise definition. By a hydrodynamic process we mean one for which the local thermodynamic variables, temperature, chemical potential (or density), and velocity, are determined by the past history of their boundary values. The normal solution to the Boltzmann equation, as well as its generalization obtained in the previous Sections, then clearly corresponds to a hydrodynamic process. The significance of the term hydrodynamic may be clarified by the consideration of some processes of non-hydrodynamic type. A process of relaxation in momentum space in a spatially uniform gas is clearly non-hydrodynamic, since the local thermodynamic variables are not at all pertinent to its description. Another example is provided by processes in a Knudsen gas. Here there is an essential dependence on the particular form of the boundary forces. An insensitivity to the nature of the boundary forces is implied in the definition of a hydrodynamic process, for which it is immaterial whether a thermal reservoir is constructed of, say, copper or aluminum, and indeed such an insensitivity has been explicitly assumed in our earlier discussion.

While the hydrodynamic ensemble (51) has now been seen to be a direct generalization of the normal solution to the Boltzmann equation, there is one important difference which merits discussion: the solution to the Liouville equation has been obtained by considering the action of the surroundings on the system, but the surroundings are usually neglected when solving the Boltzmann equation. We wish to show why the presence of external forces is necessary in one case but not in the other. Referring to Eq. (54) we first remark that the phase functions do not approach limits for infinite time, and convergence of the time integration therefore requires that the temperature, chemical potential, and velocity take on uniform values in the infinite past. Thus the hydrodynamic ensemble must reduce to equilibrium in the infinite past. Now the only solution to the Liouville equation for an *isolated* system which satisfies such an initial condition is precisely the initial equilibrium ensemble, and thus to get away from equilibrium it is necessary to introduce external interactions. (One can overlook this fact and formally derive the transport relations, as well as the Green formulae for the transport coefficients, with the Liouville equation for an isolated system. However, the ensemble thus obtained actually corresponds to equilibrium, and the "transport relations" are nothing more than the identities $0 = 0$.) Now, even with the Boltzmann equation, one should in principle imagine the existence of external forces which bring about a non-equilibrium state, since if the gas has been isolated throughout its past it will in fact be in equilibrium. However, the explicit introduction of external forces is unnecessary since the Boltzmann distribution function is a localized quantity referring to a particular point in the gas and this point may be taken to be far from the region where the external forces act. In contrast, the Gibbs distribution function refers to the system as a whole, including that part which is directly affected by the external forces.

It is, of course also, possible to obtain a description of non-equilibrium processes by examining the behavior of an isolated system subject to an initial condition imposed at a finite time. This is the procedure adopted by Mori,[20] who chooses local equilibrium as the initial condition. The resulting solution to the Liouville equation can be put into the form (51), with D given by an expression similar to (54) but with the lower limit of the time integration taken as the initial time and the time-dependence of the phase functions determined by the equations of motion for an isolated system. This approach is not an alternative to that considered here, but actually corresponds to a different physical situation. Such a situation occurs when two (or more) separated systems, each in equilibrium but at different conditions, are suddenly brought into contact. For example, a familiar method for the production of shock waves is to separate two chambers at different pressures by a diaphragm which is suddenly removed. At the instant of removal the system is clearly to be described as in a state of local equilibrium. One expects that to a considerable extent a system rapidly forgets many aspects of its past history, and there is evidence that the Navier–Stokes equations are applicable after a sufficient aging period regardless of the initial conditions. It is for this reason that the results obtained here agree with those of Mori. However, the same situation does not appear to hold for the higher order hydrodynamic equations such as the Burnett equations. Hence one should not apply such higher order equations to the decay from an arbitrary initial state, and by the same token equations obtained by considering the decay from a particular initial state cannot, beyond the Navier–Stokes approximation, be expected to apply to processes such as sound propagation which are normally generated by a driving mechanism.

We consider finally the question of irreversibility. First we comment that some aspects of irreversibility are best treated by detailed and general microscopic arguments of the sort used by Prigogine[21] and Resibois.[22] However, it is necessary to consider the role of certain well known paradoxes in the present formalism.

One aspect of irreversibility, namely an asymmetry between past and future, is introduced by a choice of a solution to the Liouville equation, that is, by our choice of the initial condition (47). There are of course other solutions: for example, one can impose the "final condition" that the system be in equilibrium at $t = +\infty$ and obtain thereby an "advanced" solution for which the time integration of Eq. (54) is altered according to

$$\int_{-\infty}^{t} dt' \to -\int_{t}^{\infty} dt' \tag{230}$$

The choice of the particular solution (54) is clearly indicated by the physical requirement that the state of the system should depend only on the past history of its surroundings.

A second aspect of irreversibility concerns the approach to equilibrium. Since this question arises only for an isolated system, we will suppose the external forces to be turned off at some time, say $t = 0$, the system then being isolated for later times. Now the Navier–Stokes equations imply an approach to equilibrium, with monotonically increasing entropy. However, for times $t > 0$ the ensemble (51) is an exact solution to the Liouville equation for an isolated system, and as is well known the quantity S' of Eq. (85) must then be time-independent and cannot approach its equilibrium value. The resolution of this paradox lies in the approximate nature of the Navier–Stokes equations, which hold only for slowly varying processes. The exact transport relations, taking into account processes of arbitrarily rapid variation, are evidently such as to maintain S' constant. One may say that the low frequency contributions to S' increase at the expense of the high frequency contributions, and measurements of a sufficiently coarse nature will show an apparent approach to equilibrium. Thus the approach to equilibrium is obtained as a natural consequence of an approximation method suited to slowly varying processes.

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QUANTUM MECHANICAL INTERPRETATION OF NUCLEAR QUADRUPOLE COUPLING DATA

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I. INTRODUCTION

The nuclei of some elements of great interest in chemistry, such as: H^2, Li^7, Be^9, B^{10}, B^{11}, N^{14}, O^{17}, Na^{23}, Al^{27}, S^{33}, Cl^{35}, Cl^{37}, Mn^{55}, Cu^{63}, Cu^{65}, Ge^{73}, As^{75}, Se^{79}, Br^{79}, Br^{81}, Sb^{121}, Sb^{123}, I^{127}, I^{129}, Cs^{133}, Hg^{201}, and Bi^{209}, have a non-spherical charge distribution with density $\rho = \rho(r,\theta,\varphi)$ which may be described in terms of a series of electrical poles of many orders. Since it may be shown that for nuclei in the ground state the dipole moment is zero, the more important terms in the series are the zero order term (monopole) and the second order term, the latter being characterized by a quadrupole moment Q.

Nuclear quadrupole resonance spectroscopy (N.Q.R.) utilizes the coupling energy between the nuclear quadrupole moment Q and the electric field gradient produced by all electrons and nuclei surrounding the quadrupolar nucleus in the molecule.

Because of this coupling energy the quadrupolar nucleus may assume a number of quantized orientations with respect to the principal direction of the field gradient. The energy involved in a transition between two levels corresponding to two such orientations may be supplied to the nucleus by the interaction between its magnetic moment and the magnetic vector of a r.f. electromagnetic field. This is possible because all nuclei with an electric quadrupole moment have also a non-zero nuclear spin (always $>\frac{1}{2}$) and therefore a magnetic moment.

Resonance is observed when the frequency of the incident radiation fulfils the Einstein's relation:

$$\nu = \frac{E_2 - E_1}{h} \tag{1}$$

where E_2 and E_1 are the energies of the quadrupole in the orientations 1 and 2.

More precisely, it is possible to show that the hamiltonian of the energy of the nuclear quadrupole moment in the field produced by the electrons and the other surrounding charges is:

$$H = \frac{eQ}{2I(2I - 1)} [V_{xx}I_x^2 + V_{yy}I_y^2 + V_{zz}I_z^2] \tag{2}$$

where $V_{xx} = \partial^2 V/\partial x^2$, etc. are the components of the electric field gradient, I is the nuclear spin number and Q is the nuclear quadrupole moment; x, y, z are the axes of a reference system orientated in such a way that the cross terms of the field gradient tensor vanish.

In Eq. (2) the three components of the electric field gradient are not independent; they are related by the Laplace equation, which, in this instance, takes the form:

$$V_{xx} + V_{yy} + V_{zz} = 0 \tag{3}$$

since one can approximate so that all the electronic charges which generate the electric field are external to the nucleus. Therefore the hamiltonian in Eq. (2) depends only on two of the three components of the field gradient.

Such nuclei as Cl^{35}, Br^{79}, Br^{81}, I^{127} have, so far, been particularly used in N.Q.R. spectroscopy.

Since the atoms containing the above-mentioned nuclei are bonded in the molecules with only a single bond, it may be assumed, in a first-order approximation, that the field gradient in the vicinity of the nucleus has a nearly cylindrical symmetry, i.e., $V_{xx} \simeq V_{yy}$. It is then convenient to define a quantity η called the "asymmetry parameter":

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \tag{4}$$

which gives a measure of the deviation of the field gradient from the cylindrical symmetry.

By use of Eqs. (3) and (4) the hamiltonian may thus be written as follows:

$$H = \frac{eQV_{zz}}{4I(2I-1)} [2I_z^2 - (1-\eta)I_x^2 - (1+\eta)I_y^2] \tag{5}$$

Equation (5) contains only the component along the z axis of the field gradient and the asymmetry parameter η.

The solution of the quantum mechanical problem corresponding to Eq. (5) is particularly easy in the case of cylindrical symmetry ($\eta = 0$). The energy levels of the nucleus in the field gradient are then:

$$E_M = \frac{eQV_{zz}}{4I(2I-1)} [3M_I^2 - I(I+1)] \tag{6}$$

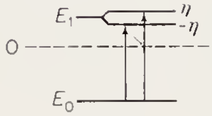
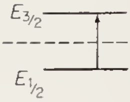
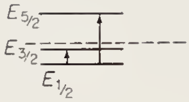
where $M_I = I, I-1, \cdot \cdot \cdot -I$.

In the case of deviation from cylindrical symmetry ($\eta \neq 0$) the solution becomes more complicated. However, if the parameter η is not too large ($\eta < 0.5$), as is often the case, it is possible to solve the problem by using the perturbation theory.[5]

A representation of the energy levels and of the transitions in some typical cases is given in Table I.

It may be noticed that both V_{zz} and η values may be obtained (with the exception of nuclei with spin = 3/2) from the measurement of two resonance frequencies. When the nuclei have spin $I = 3/2$, and only one frequency is observed, further information

TABLE I

$I = 1$	$I = \frac{3}{2}$	$I = \frac{5}{2}$
		
$\nu_1 = \frac{3eQ}{4}\left(\frac{\partial^2 V}{\partial z^2}\right)(1+\eta)$ $\nu_2 = \frac{3eQ}{4}\left(\frac{\partial^2 V}{\partial z^2}\right)(1-\eta)$	$\nu = \frac{1eQ}{2}\left(\frac{\partial^2 V}{\partial z^2}\right)\left(1+\frac{\eta^2}{3}\right)^{\frac{1}{2}}$	$\nu_1 = \frac{3eQ}{20}\left(\frac{\partial^2 V}{\partial z^2}\right)[1+1.296\eta^2 - 0.55\eta^4]$ $\nu_2 = \frac{6eQ}{20}\left(\frac{\partial^2 V}{\partial z^2}\right)[1-0.2037\eta^2 + 0.18\eta^4]$
^{14}N ^{6}Li ^{2}H	^{35}Cl ^{37}Cl ^{79}Br ^{81}Br ^{11}B	^{127}I ^{17}O

may be obtained from the Zeeman splitting of the frequency in a single crystal of the substance under examination.

Once V_{zz} and η are known, V_{xx} and V_{yy} may also be calculated from Eqs. (3) and (4):

$$\begin{aligned} V_{xx} &= -\left(\frac{1-\eta}{2}\right)V_{zz} \\ V_{yy} &= -\left(\frac{1+\eta}{2}\right)V_{zz} \end{aligned} \tag{7}$$

It may be noticed that in all the expressions of Table I the quantity (eQV_{zz}) appears which is generally called the "quadrupole coupling constant." This is also written in the form (e^2Qq_{zz}), if $V_{zz} = eq_{zz}$.

The principal aim of the theoretical work which is being done in this field is to compute the quadrupole coupling constant directly from the molecular wave function. The electric field gradient at the quadrupolar nucleus is produced by the electrons and surrounding nuclei, so that comparison of the experimental value of the coupling constant with the value calculated from any wave function which may be reasonably assumed is a very useful test for the same wave function. Such a test may be used together with others (e.g., comparison between experimental and calculated values of the dipole moment, bond energy, etc.) to check the hypothesis about the electronic structure of the molecule under investigation.

II. ELECTRIC FIELD GRADIENT PRODUCED BY ALL THE CHARGED PARTICLES PRESENT IN THE MOLECULE

The potential function $V(r_i)$ produced by the ith point charge (nucleus or electron) located at the distance r_i from the quadrupolar nucleus is:

$$V(r_i) = Z_i e/r_i \quad (Z_i = -1 \text{ for an electron}) \tag{8}$$

therefore, in the chosen Cartesian coordinates system, the overall electric field gradient along the z axis, may be written:

$$\begin{aligned} eq_{zz} &= \frac{\partial^2 V}{\partial z^2} = \sum_i \frac{\partial^2 V(r_i)}{\partial z_i^2} \\ &= \sum_i \frac{\partial^2}{\partial z_i^2} [Z_i e(x_i^2 + y_i^2 + z_i^2)^{-\frac{1}{2}}] = \sum_i Z_i e \left(\frac{3\cos^2\theta_i - 1}{r_i^3}\right) \end{aligned} \tag{9}$$

where θ_i is the angle between the z axis and the radius vector r_i. Once the wave function Ψ for the ground state of the molecule is known, the field gradient is:

$$\langle eq_{zz} \rangle = \sum_i Z_i e \int \Psi^\star \left(\frac{3\cos^2\theta_i - 1}{r_i^3}\right) \Psi \, d\tau \tag{10}$$

A. The Theory of Townes and Daily

The general theory of the quantum mechanical interpretation of the quadrupole resonance data was originally formulated by Townes and Daily[42] in a pioneer paper in 1949, which has been the basis for most of the subsequent work.

In the original theory of Townes and Daily, in order to simplify Eq. (10), several reasonable assumptions are made which also stress the essential terms of the problem. The electric charges of a molecule are divided into three groups: (*a*) the electrons of the closed shells of the atom bearing the quadrupolar nucleus, which are supposed to be unperturbed; (*b*) the valence electrons of the same atom; (*c*) the electrons and nuclei of all the other atoms of the molecule. The contribution of the electrons of group (*a*) to the field gradient is assumed to be zero because of the symmetry of the closed shells. The contribution of any charge external to the atom is neglected as it is small because of a partial compensation between electronic and nuclear charges and of the factor $1/r^3$ in Eq. (10). The only term remaining is the contribution of the valence shell electrons (all s electrons are again excluded because of the spherical symmetry of their distribution).

Assuming hydrogenoid orbitals for these electrons, the contribution, to the field gradient, of an electron with quantum numbers n, l, m, with, for instance, $m = 0$, $\pm l$ $(l \neq 0)$, is the following:

$$\begin{aligned} eq_{n,l,m=0} &= \frac{4e^2Z^3}{n^3a_0^3(2l-1)(2l+1)(2l+3)} \\ eq_{n,l,m=\pm l} &= -\frac{2l-1}{l+1}\,q_{n,l,m=0} \end{aligned} \qquad \text{(i)}$$

These relations show that the field gradient decreases very rapidly when the quantum numbers n and l become large; therefore, for a valence shell with principal quantum number n, the contributions of the electrons in the p orbitals $(l = 1)$ are preponderant and, in this theory, the contribution of the remaining electrons is neglected.

If the bond axis is taken as the z axis, the preceding relationships show that for the p-type electrons we have $eq_x = eq_y = -\frac{1}{2}eq_z$. Then if n_x, n_y, n_z are the occupation numbers of the p_x, p_y, and p_z orbitals respectively, the field gradient due to all p electrons of the shell is:

$$eq = n_x(eq_x) + n_y(eq_y) + n_z(eq_z) = \left(n_z - \frac{n_x + n_y}{2}\right)eq_z \qquad \text{(ii)}$$

When the atom is part of a molecule, substantial changes of the occupation numbers n_x, n_y, and n_z occur with respect to those existing in the free atom (and corresponding changes of the field gradient will occur also). These changes are closely dependent on the nature of the bond between the atom bearing the quadrupolar nucleus and the rest of the molecule. In the theory of Townes and Daily such variations are calculated by an adequate description of the valence shell of the atom in the molecule. Let us take, as an example, a halogen atom in an organic molecule. In this theory the seven valence-shell electrons of this atom are placed in a set of orthogonal atomic orbitals, namely: one electron in a digonal hybrid bond orbital of the s–p–d type, with direction along the bond axis; one of the three lone pairs in a second digonal hybrid orthogonal to the first, and finally the two remaining pairs are placed in the two p_x and p_y orbitals, orthogonal to the bond axis.

Let s and d be the hybridization parameters which define the digonal hybrid bond orbital, i the ionicity parameter of the bond, and π the eventual double-bond character; the field gradient is then found to be:

$$(eq)_{\mathrm{mol}} = [(1 - s^2 + d^2 \pm i - \pi) \pm i(s^2 + d^2)](eq_z)_{\mathrm{atom}} \qquad \text{(iii)}$$

It is easily seen that this theory permits direct information about the essential features of the bond, such as the ionicity i and the hybridization of the atomic functions, to be obtained, once the ratio $\rho = (e^2Qq)_{\mathrm{mol}}/(e^2Qq)_{\mathrm{atom}}$ between the resonance frequency of the molecule and that of the free atom is experimentally determined.

It has largely been shown that the various simplifications introduced by this elegant theory do not alter substantially the correctness of the interpretation of the quadrupole coupling constant and that the theory itself is the starting point of a systematic research which will enable us to obtain more and more detailed information about the electronic configuration of the molecules in the ground state by quadrupole spectroscopy. Many examples of the use of this theory can be found in the books by Townes and Schawlow,[41] Gordy, Smith, and Trambarulo,[9] and Das and Hahn.[4]

For a general and more detailed interpretation of the results of N.Q.R. spectroscopy, it may be useful to recall the general features of the calculation of an observable quantity in a many-particle quantum mechanical system.

III. THE QUANTUM MECHANICAL CALCULATION OF AN OBSERVABLE QUANTITY IN THE MANY-PARTICLE SYSTEMS

Some aspects of the *ab initio* calculation of an observable quantity such as the quadrupole coupling constant in an isolated molecule, i.e. influenced by no external action, will be discussed here. Such a calculation is strictly applicable only to a molecule in the gaseous state and, in order to extend it to solids, on which N.Q.R. experiments are usually carried out, some corrections are necessary because of intermolecular effects in the crystals.

The theory of many-particle systems which uses the "density matrix" technique is suitable for this purpose. We will assume throughout the present exposition the non-relativistic approximation.

In the quantum mechanics of Schrödinger, once the eigenfunction $\Psi_m = \Psi_m(x_1, x_2, \cdots, x_N)$* (solution of the equation $\mathbf{H}\Psi = E\Psi$ for the mth stationary state of the N-particle system of the molecule) is known, any observable property A of the mth state is calculated by associating with the observable A an operator $\mathscr{A}$ and computing its average value with the operation:

$$\langle \mathscr{A} \rangle = \int \Psi_m^\star(x_1, x_2, \cdots, x_N)\mathscr{A}\Psi(x_1, x_2, \cdots, x_N)dx_1 \cdots dx_N \quad (11)$$

In quantum mechanical problems concerning molecules, because of their complexity due to the large number of particles, several simplifying assumptions are made. The first (which we will indicate, throughout this paper, as (a)) is the Born–Oppenheimer assumption. It allows the motion of the n electrons to be separated from the much slower motion of the $N - n$ nuclei by considering all nuclei as fixed and studying only the motion of the electrons in the field generated by any configuration of the nuclei.

It is then possible to write: $\Psi = \Psi_N\Psi_e$, where the electronic part $\Psi_e = \Psi_e(x_1, x_2, \cdots, x_n)$ (in which the coordinates of the nuclei enter only as fixed parameters and are not explicitly written) is antisymmetric with respect to any exchange of the electron coordinates, i.e., it fulfils the condition:

$$\mathbf{P}\Psi_e(x_1, x_2, \cdots, x_n) = (-1)^p\Psi_e(x_1, x_2, \cdots, x_n) \quad (12)$$

where $\mathbf{P}$ is a permutation operator with parity p which operates on the indexes of the n coordinates x_i.

An examination of the remaining approximations will be made later since now it is convenient to introduce the notations concerning the density matrix.

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* $x_i \equiv x_i, y_i, z_i, \sigma_i$ represents the set of the position and spin coordinates of the ith particle.

Many authors have shown[6,11,13,15,16,17,20] that for any stationary state of a system with many identical particles it is possible to define a series of density matrices of the various orders which allow the average value of any operator $\mathscr{A}$ to be calculated in a more direct way than by the use of the eigenfunctions of Eq. (11).

In the Born–Oppenheimer approximation (omitting, for simplicity, the index e of the electronic eigenfunction), the density matrices relative to the n electrons of the molecule are:

$$\gamma(x_1'|x_1) = n\int \Psi^\star(x_1', x_2, \cdots, x_n)\Psi(x_1, x_2, \cdots, x_n)\, dx_2 \cdots dx_n$$

$$\begin{aligned}\Gamma(x_1'x_2'|x_1x_2) &= \frac{n(n-1)}{2}\int \Psi^\star(x_1', x_2', x_3, \cdots, x_n)\Psi(x_1, x_2, \cdots, x_n)\, dx_3 \cdots dx_n \\ &\cdots\cdots\cdots\cdots \\ \Gamma(x_1'x_2' \cdots x_p'|x_1x_2 \cdots x_p) &= \binom{n}{p}\int \Psi^\star(x_1', x_2', \cdots, x_p', x_{p+1}, \cdots, x_n)\Psi(x_1, x_2, \cdots, x_p, \cdots, x_n)\, dx_{p+1} \cdots dx_n\end{aligned} \tag{13}$$

The diagonal elements of the matrices (13) have a direct physical meaning: for instance, for the first order density matrix $\gamma(x_1'|x_1)$, from the definition (13) one obtains $\int\gamma(x_1|x_1)dx_1 = n$. Then $\gamma(x_1|x_1)dx_1$ results equal to n times the probability of finding *a* whatever electron of the system in the volume element dx_1, which defines its position and its spin state. The extension of the physical meaning to the higher order density matrices is trivial.

When the density matrices (13) are known, the average value of an operator $\mathscr{A}_p$ which involves p particles is obtained by the integral:

$$\langle\mathscr{A}_p\rangle = \int \mathscr{A}_p\Gamma(x_1'x_2' \cdots x_p' \cdots x_p)\, dx_1 \cdots dx_p \tag{14}$$

where the operation $\mathscr{A}_p$ is first carried out only on the non-primed coordinates, and then the substitution $x_i' = x_i$ $(i = 1, 2, \cdots, p)$ is made before integrating. In this formulation only the minimum number of distinct electronic coordinates appears explicitly.

In this scheme the calculation of the quadrupole coupling constant is reduced to the calculation of the following expression:

$$\langle eq_{zz}\rangle = -e\int\left(\frac{3\cos^2\theta_{A1}-1}{r_{A1}^3}\right)\gamma(x_1|x_1)\,dx_1+\sum_{\alpha}Z_\alpha e\left(\frac{3\cos^2\theta_{A\alpha}-1}{R_{A\alpha}^3}\right) \tag{15}$$

where θ_{A1} is the angle between the z axis and the radius vector r_{A1} connecting the quadrupolar nucleus A and the generical electron 1; $\theta_{A\alpha}$ is the analogous angle (also referred to the z axis) for the nucleus α; Z_α and $R_{A\alpha}$ are respectively the electric charge and the distance of the nucleus α from the quadrupolar nucleus A.

The only approximation introduced in writing the density matrices in Eq. (13) is that of Born–Oppenheimer, which, for the calculation of several molecular quantities, is a very good one.

A more explicit form of the density matrices requires a more detailed knowledge of the form of the eigenfunction.*

The most suitable many-electron molecular wave functions are the antisymmetrized products (Slater's determinants) of mono-electronic wave functions, and it may be shown[14] that any anti-symmetric wave function $\Psi = \Psi(x_1, x_2, \cdots, x_n)$ may always be expanded in a series of such determinants:

$$\begin{aligned}\Psi(x_1, x_2, \cdots, x_n)\\ &= (N!)^{-\frac{1}{2}}\sum_{k,l,m} c_{k,l,m\ldots}\det\{\varphi_k(x_1)\varphi_l(x_2)\cdots\varphi_\nu(x_n)\}\end{aligned} \tag{16}$$

The n functions φ_k which appear in each determinant of Eq. (16) are chosen from a discrete, orthonormal and complete set of mono-electronic wave functions (spin orbitals) and the summation is over all possible choices.

Now we may go on with the list of the principal simplifications which are assumed in the study of the actual molecular problems, besides the already cited Born–Oppenheimer assumption (*a*).

(*b*) The expansion (16) is interrupted retaining only some properly chosen terms (for instance, by using the so-called Löwdin's "natural spin orbitals"). More often, only one Slater's determinant is retained, in which the φ_k functions are molecular orbitals obtained by self-consistence methods.* In the last instance it is easily seen[15] that the density matrices have the particularly simple form:

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* The following treatment obtains the density matrices by explicitly using the wave functions but several authors have shown that this is not strictly necessary.

$$\gamma(x_1'|x_1) = \sum_k \varphi_k^\star(x_1')\varphi_k(x_1)$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\Gamma(x_1'x_2'\cdots x_p'|x_1x_2\cdots x_p) = \frac{1}{p!}\begin{vmatrix} \gamma(x_1'|x_1)\gamma(x_1'|x_2)\cdots\gamma(x_1'|x_p) \\ \cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots \\ \gamma(x_p'|x_1)\gamma(x_p'|x_2)\cdots\gamma(x_p'|x_p) \end{vmatrix} \tag{17}$$

and therefore, for the calculation of the matrices of the various orders in this approximation, it is only necessary to know $\gamma(x_i'|x_j) = \sum_k \varphi_k^\star(x_i')\varphi_k(x_j)$.

(*c*) The hamiltonian operator is usually written:

$$\mathbf{H} = \sum_i\left(-\frac{1}{2}\nabla_i^2\right) - \sum_i\sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + \frac{1}{2}\sum_i\sum_{j\neq i}\frac{1}{r_{ij}} \tag{18}$$

where $r_{i\alpha}$ is the distance between the electron i and the nucleus α and r_{ij} is the distance between the electron i and electron j. In this operator the quadrupolar component of the potential energy due to the quadrupole moment of the nuclei (for which this is not zero) is not included† and all spin–spin and spin–orbit interactions are also neglected. In this last approximation the molecular spin-orbitals may be factorized into a space part $\varphi_k(q_i)$ $(q_i \equiv x_i, y_i, z_i)$ and a spin part $\alpha(\sigma_i)$ or $\beta(\sigma_i)$.

---

* Retaining only one determinant is a drastic simplification, but it may be partially compensated by introducing a suitable "correlation factor" $g(r_{12}, r_{13}, r_{23}, \cdots)$ containing explicitly the interelectronic distances. The results thus far obtained for two-electron systems are encouraging[33] but the extension to many-particle problems has been very little explored. (For a more extended treatment see Löwdin.[18]) In the following treatment the correlation effect is not considered.

† This term of the energy produces a polarization of the inner electrons which results in a deviation from spherical symmetry of the field experienced by the valence electrons. The effect of this is an appreciable change of the quadrupole coupling constant. Sternheimer[37–40] showed that the effect of the polarization of the inner shell electrons on the quadrupole coupling constant can be taken care of by multiplying the same constant by a correction factor $1 - R$, which may be obtained by perturbation methods.

(*d*) The positional parts of the molecular spin-orbitals are written as linear combinations:

$$\varphi_k = \sum_r c_{rk}\chi_r \tag{19}$$

of a suitable set of atomic orbitals χ_r (in general non-orthogonal) centered on the atoms of the molecule and containing a finite number of variational parameters (in general one: the effective charge).

(*e*) A set of nodeless Slater's functions of the following type:

$$\chi_i = N_i r^{n_i - 1} \exp\,(-\zeta_i r) S_l^m(\theta,\varphi) \tag{20}$$

containing only one variational parameter is used as basic set of atomic orbitals.

(*f*) Because of the simple form (18) of the hamiltonian, a last approximation can be adopted: in the molecules with an even number of electrons, the ground state of which is a singlet state, the $n = 2\nu$ electrons are arranged in pairs, with antiparallel spins, in the ν molecular orbitals of lowest energy. This is a simple way of making the function represent a state of pure spin.[18]

(*g*) If one adopts the approximations (*c*) and (*f*), then it is possible to integrate the density matrices with respect to the spin coordinates of the electrons and to introduce the "spinless density matrices":

$$\begin{aligned} \gamma(q_1'|q_1) &= \int [\gamma(x_1'|x_1)]_{\sigma_1'=\sigma_1}\, d\sigma_1 = 2\sum_k \varphi_k^\star(q_1')\varphi_k(q_1) \\ \Gamma(q_1'q_2'|q_1q_2) &= \int [\Gamma(x_1'x_2'|x_1x_2)]_{\substack{\sigma_1'=\sigma_1\\ \sigma_2'=\sigma_2}}\, d\sigma_1 d\sigma_2 = \frac{1}{2}\begin{vmatrix} \gamma(q_1'|q_1)\gamma(q_1'|q_2) \\ \gamma(q_2'|q_1)\gamma(q_2'|q_2) \end{vmatrix} \\ &\cdots\cdots\cdots\cdots \end{aligned} \tag{21}$$

Let us suppose that all simplifying assumptions (*a*) through (*g*) have been adopted; i.e. the wave function for the n electrons is formed by only one Slater's determinant and the mono-electronic functions φ_k have the following properties: (1) they form an orthonormal set, (2) they are filled by two electrons, (3) they have the form of Eq. (19).

From Eq. (21) one deduces for $\gamma(q_1'|q_1)$:

$$\gamma(q_1'|q_1) = 2\sum_r\sum_s\Big(\sum_k c_{rk}^\star c_{sk}\Big)\chi_r^\star(q_1')\chi_s(q_1) = 2\sum_r\sum_s R_{rs}\chi_r^\star(q_1')\chi_s(q_1) \qquad (22)$$

In this expression, besides the matrix **C** of the coefficients, defined in Eq. (19), the matrix $\mathbf{R} = \mathbf{cc}^\dagger$ has been introduced, the elements of which are $R_{rs} = \sum_k c_{rk}^\star c_{sk}$.

If the basic atomic functions χ_r are not orthogonal, we get: $\int \chi_r^\star \chi_s \, dq = S_{rs} \neq \delta_{rs}$. Then, by integration of Eq. (22) one obtains*:

$$\int \gamma(q_1'|q_1)\, dq_1 = 2\sum_r\sum_s R_{rs}S_{rs} = 2 \operatorname{tr} \mathbf{RS} = n \qquad (23)$$

or:

$$\sum_r\sum_s \mathscr{P}_{rs} = n \qquad (24)$$

where a new $\mathscr{P}$ matrix ("population matrix") has been introduced, the elements of which are:

$$\mathscr{P}_{rs} = 2R_{rs}S_{rs}$$

This result allows an immediate physical visualization; Eqs. (23) and (24) subdivide the space in the molecule into a mosaic of distinct elements (corresponding to the normalized functions $\chi_r^\star\chi_r$ and $\chi_r^\star\chi_s/S_{rs}$) and indicate how the electrons are distributed in them. The diagonal elements $\mathscr{P}_{rr}$ have been named[23–26] "net orbital populations"† and the $\mathscr{P}_{rs}$ elements "overlap populations".

By using Eq. (22) for the first-order density matrix and recalling Eq. (14), any mono-electronic observable property‡ of the molecule is calculated by means of the equation:

$$\langle \mathscr{A} \rangle = 2\sum_r\sum_s R_{rs}A_{rs} = 2 \operatorname{tr} \mathbf{RA} \qquad (25)$$

---

* **R** and **S** are Hermitian matrices.

† In orientative calculations it may be useful to consider, besides the net orbital population, the "gross orbital populations" $\bar{\mathscr{P}}_{rr} = \mathscr{P}_{rr} + \Sigma_{s\neq r}\mathscr{P}_{rs}$, which are obtained by adding one half of the overlap populations of χ_r and all the other orbitals to the net population of the χ_r orbital (i.e. by summing all elements of the rth row of the matrix).

‡ The extension to the calculation of poly-electronic properties is not difficult since, in the present approximation, the density matrices of higher order take the rather simple form (21).

where

$$A_{rs} = \int \chi_r^{\star} \mathscr{A} \chi_s \, dq$$

In particular, the field gradient may be written, recalling Eq. (15):

$$\begin{aligned} eq_{zz} &= 2\sum_r\sum_s eR_{rs}\int\left(\frac{3\cos^2\theta_{A1}-1}{r_{A1}^3}\right)\chi_r^{\star}(q_1)\chi_s(q_1)\,dq_1 \\ &\qquad\qquad + \sum_\alpha Z_\alpha e\left(\frac{3\cos^2\theta_{A1}-1}{R_{A\alpha}^3}\right) \\ &= 2e \operatorname{tr} \mathbf{Rq} + e\sum_\alpha Z_\alpha\left(\frac{3\cos^2\theta_{A\alpha}-1}{R_{A\alpha}^3}\right) \end{aligned} \tag{26}$$

In this equation q is a matrix, the elements of which are:

$$q_{rs} = \int\left(\frac{3\cos^2\theta_{A1}-1}{r_{A1}^3}\right)\chi_r^{\star}(q_1)\chi_s(q_1)\,dq_1 \tag{27}$$

and may easily be calculated once the set of basic atomic orbitals χ_r has been chosen.

McWeeny[20] has shown that it is possible to compute directly the **R** matrix for the ground state of the molecule without calculating the molecular orbitals (19) and the matrix **C**; we will therefore directly use Eq. (26) in the description of some examples without any further comment about the calculation of the matrix **R**.

A. Wave Functions for Diatomic Molecules

Only a very small number of many-electron molecules has been studied so far, at least in the only limits of the approximations (*a*)–(*g*). Very noteworthy is the systematic work carried out at the Molecular Structure Laboratory of the University of Chicago. The results obtained in that laboratory concerning the diatomic molecules of the elements of the first row of the periodic system have been published.[29,30]

These molecules have been studied by using only one term of the expansion (16) and with Slater-type functions as basic atomic orbitals, with the following approximations:

(i) Fixed values of the ζ parameter, calculated by the known Slater's rules.

(ii) Fixed values of ζ equal to the values which minimize the energy of each isolated atom (Best Atomic ζ, B.A.).

(iii) Values of ζ which minimize the total molecular energy (Best Limited Molecular ζ, B.M.). (In this last treatment CO, BF, and LiF molecules are excluded.)

The conclusions of this research are: (1) in all the three approximations the average difference between calculated and experimental total energies is within 1%. (2) The absolute errors are still too large (e.g. for the molecules of CO and N_2 they are of the order of one a.u.) to allow a reasonable calculation of the dissociation energy. (3) The direction given for the electric dipole moment agrees with the experimental results in the few instances in which the latter is known, although very often the numerical values differ appreciably from the experimental values. (4) The approximation (iii) always leads to a better value of the energy, as expected.

B. Examples: CO^{17} and N_2 Molecules

The detailed analysis of some examples shows clearly the degree of approximation which can be achieved today and suggests the improvements which must be introduced in the calculation of the molecular wave functions.

Let us start with the CO^{17} molecule, for which Rosenblum and Nethercot[33] give the value $eq_O = -0.64$ a.u. According to Eq. (26) this value corresponds to the total field gradient produced by all the electrons of the molecule and by the carbon nucleus at the point where the O^{17} nucleus is centered.

For comparison purposes it is useful to consider also the contribution of the electrons alone $eq^0_{el} = eq^0 - 2eZc/R^3 = -0.64 - 1.24 = -1.88$ a.u.

By using the self-consistent orbitals obtained by B. J. Ransil[30] all necessary terms for the evaluation of the electronic part of the field gradient may be calculated.

The basic atomic functions used by this author are Slater-type orbitals of the two atoms: $1s_O$, $2s_O$, $2p_{\sigma O}$, $2p_{\pi O}$, $2p_{\bar{\pi} O}$; $1s_C$, $2s_C$, $2p_{\sigma C}$, $2p_{\pi C}$, $2p_{\bar{\pi} C}$, in the approximation (i) and (ii) of this chapter. Since the results obtained in the two approximations do not differ substantially we will refer to the case (i) only.

In Table II are reported, in a compact form, the four matrices,

TABLE II

	$1s_O$	$2s_O$	$2p_{\sigma O}$	$1s_C$	$2s_C$	$2p_{\sigma C}$	$2p_{\pi O}$	$2p_{\pi C}$	$2p_{\bar{\pi} O}$	$2p_{\bar{\pi} C}$	$\sum_s P_{rs} S_{rs}$
$1s_O$	2.10832 0 0	−0.45052 0 0	0.07402 0 0	0.01178 −0.00060 −0.00001	0.02220 −0.04068 −0.00090	−0.07054 −0.07915 0.00558					1.9985
$2s_O$	−0.45052 0 0	2.00786 0 0	−0.52228 0 0	−0.00418 −0.01377 0.00006	−0.28364 −0.06198 0.01758	0.12714 −0.09730 −0.01237					1.84567
$2p_{\sigma O}$	0.07402 0 0	−0.52228 0 0	1.28980 −3.140 −4.050	−0.11646 −0.02317 0.00270	0.12694 −0.22865 −0.02902	0.65568 −0.36035 −0.23627					1.51582
$1s_C$	0·01178 −0.00060 −0.00001	−0.00418 −0.01377 0.00006	−0.11646 −0.02317 0.00270	2.09476 −0.20580 −0.43110	−0.39196 −0.04548 0.01783	0.11190 −0.02011 −0.00225					1.99871
$2s$	0.02220 −0.04068 −0.00090	−0.28364 −0.06198 0.01758	0.12694 −0.22865 −0.02902	−0.39196 −0.04548 0.01783	1.84410 −0.12450 −0.22959	−0.70438 −0.10039 0.07071					1.68050
$2p_{\sigma C}$	−0.07054 −0.07915 0.00558	0.12714 −0.09730 −0.01237	0.65568 −0.36035 −0.23627	0.11190 −0.02011 −0.00225	−0.70438 −0.10039 0.07071	0.70632 −0.21077 −0.14887					0.95748
$2p_{\pi O}$							1.18960 1.570 1.868	0.72286 0.04544 0.03285	0 0 0	0 0 0	1.3736
$2p_{\pi C}$							0.72286 0.04544 0.03285	0.43924 −0.08137 −0.03574	0 0 0	0 0 0	0.6242
$2p_{\bar{\pi} O}$							0 0 0	0 0 0	1.18960 1.570 1.868	0.72286 0.04544 0.03285	1.3736
$2p_{\bar{\pi} C}$							0 0 0	0 0 0	0.72286 0.04544 0.03285	0.43924 −0.08137 −0.03574	0.6242

of which the elements are respectively: $2R_{rs}$, q_{rs}, $2R_{rs}q_{rs}$; in each location the sequence of the elements is the following:

$$\boxed{\begin{array}{c} 2R_{rs} \\ q_{rs} \\ 2R_{rs}q_{rs} \end{array}}$$

In the column to the right the "gross population" $\mathscr{P}_{rr} + \sum_{s \neq r} \mathscr{P}_{rs}$ for each atomic orbital is reported.

The value of the electronic contribution to the field gradient calculated from these data is $eq^0_{el} = -1.396$ a.u., which is 74% of the experimental value.

This result is to be considered not too bad owing to the complexity of a 14-electron problem such as that of the CO molecule and also because of the great sensitivity of the field gradient to the form of the wave functions. It does not allow, however, a reasonably accurate *ab initio* calculation of eq^0, since this value, which results from the difference of two comparable quantities such as eq^0_{el} and $2eZc/R^3$ (this latter is indeed, practically exact), contains a much greater percentage error than that contained in the two terms separately. In fact, one finds: $eq^0 = eq^0_{el} + 2eZc/R^3 = -0.16$ a.u., which is only 25% of the experimental value.

From Table II, the contribution of the electronic population of the oxygen orbitals $q_{\text{O,OO}}$, the contribution of the overlap population $q_{\text{O,OC}}$ and that of the populations localized in the carbon orbitals $q_{\text{O,CC}}$, are respectively found to be:

$$\left.\begin{cases} q^{\sigma}_{\text{O,OO}} = -4.050 \\ q^{\pi}_{\text{O,OO}} = +3.736 \end{cases}\right\} q_{\text{O,OO}} = -0.314$$

$$\left.\begin{cases} q^{\sigma}_{\text{O,OC}} = -0.505 \\ q^{\pi}_{\text{O,OC}} = +0.131 \end{cases}\right\} q_{\text{O,OC}} = -0.374$$

$$\left.\begin{cases} q^{\sigma}_{\text{O,CC}} = -0.637 \\ q^{\pi}_{\text{O,CC}} = -0.071 \end{cases}\right\} q_{\text{O,CC}} = -0.708$$

These values show that the contributions of the overlap and carbon orbitals populations, which are further away than all other populations from the oxygen nucleus, are not negligible. Moreover (as has been shown in detail by Richardson[31]) these contributions do not compensate the effect of the carbon nucleus.

It may also be noticed that the contributions of the $2p^{\sigma}_{O,OO}$ and $2p^{\pi}_{O,OO}$ orbital populations to the field gradient are far greater than all others, although in the final calculation they partially compensate each other because of their opposite sign; it is therefore expected that the final result will be particularly sensitive to the shape of these functions and that better results can only be obtained by an *ab initio* calculation (still using the approximations (*a*)–(*g*)), by using sufficiently flexible basic atomic functions, which may give the correct value of the field gradient for both the free atom and the molecule.

In the case of CO^{17} the rather poor result may be partially explained by noting that the Slater's atomic orbitals with constant values of zeta are a very crude approximation; in the atomic oxygen they give a value $eq^{0}_{p_z} = -(4/15)\zeta^3 = -3.14$ a.u. (best atom: $eq^{0}_{p_z} = -2.942$ a.u.) while the value reported by Yamanouchi and Horie[43] is -3.98 a.u.; it may then be presumed that a more suitable set of basic functions will lead to a better result.

An accurate analysis on this point was made by Richardson[31] for the N_2 molecule and leads to very interesting conclusions. This author calculated the field gradient by using the Ransil's molecular orbitals in the approximation (i) (zeta constant), (iii) (zeta varied in the molecule), and a new type of molecular orbital [approximation (iv)] with a more extended basis, in which each atomic orbital 2*s* and 2*p* of the nitrogen atom is composed of two Slater-type functions with different zeta parameters (double zeta approximation).

When the variational calculus is carried out to minimize the energy in the molecule [as in approximation (iii)] different values are obtained for ζ_σ and ζ_π; for instance, for nitrogen in N_2 it is found that $\zeta_{2p_\sigma} = 2.2524$ and $\zeta_{2p_\pi} = 1.9090$ while the Slater's values for the free atom are $\zeta_{2p_\sigma} = \zeta_{2p_\pi} = \zeta_{2p} = 1.95$. Such a difference leads to a greater expansion of the $2p_\pi$ orbital with respect to the $2p_\sigma$ orbital in the formation of the molecule. Moreover, as noted by Richardson, because of the cubic dependence of the field gradient on ζ, very marked differences of the corresponding values of $eq_{A,AA}$ result compared to those obtained when all ζ values are equal. It is, in fact, easy to see that:

$$\begin{aligned}\Delta(eq_{A,AA}) &= \Delta[P_\sigma(eq_\sigma) + 2P_\pi(eq_\pi)] \\ &\simeq 3eq^0_{A,AA}\left[P_\sigma\frac{\Delta\zeta_\sigma}{\zeta_0} - 2P_\pi\frac{\Delta\zeta_\pi}{\zeta_0}\right] \qquad (28)\end{aligned}$$

where the change in the orbital populations has been neglected and $eq^0_{A,AA}$ is the value obtained with $\zeta_\sigma = \zeta_\pi = \zeta_0$, i.e. the value in the free atom, and $P = 2R$.

In the nitrogen molecule $\Delta(eq_{A,AA})$, according to Richardson, amounts to about -0.93 a.u., the change in $q_{N,NN}$ being from -0.397 to -1.327 a.u.

Analogous strong changes in $eq_{A,AA}$ are obtained in approximation (iv) with respect to the approximation where only one Slater's function is used to describe each atomic orbital. This is because the larger number of basic orbitals gives the function more flexibility, resulting in a better approximation to the best shape.

In treating nitrogen, Richardson makes use of the experimental value of $e^2qQ = -4.65$ MH (obtained from solid nitrogen at 4.2° K) and of the calculated value of eq to find the quadrupole moment Q. In the three approximations (i), (iii), and (iv) he obtains: $Q_N = 0.064 \times 10^{-24}$, 0.015×10^{-24}, and 0.019×10^{-24} cm^2 respectively. These values are in a progressively better agreement with the value $Q_N = 0.02 \times 10^{-24}$ reported by Townes and Schawlow[41] and show a progressive improvement of the wave function.

On the basis of these results it is reasonable to hope that the use of the approximations (iii) and (iv) for CO^{17} and the other diatomic molecules will improve the agreement with the more important experimentally measurable quantities. It is then very likely that workers in this field will devote, in the near future, much attention to the improvement of the basic functions, by increasing their number and their flexibility.

On the other hand, the enlargement of the basic set of atomic orbitals is indispensable when Slater-type nodeless functions are used. In fact, the atomic functions $2s$, $3p$, $4d$; $3s$, $4p$, $5d$;

4*s*, 5*p*, 6*d*, etc., which have an increasing number of nodes, may be reproduced with sufficient accuracy only by combining an adequate number of Slater's orbitals.[14,36]

In Fig. 1 the radial part of the 3*p* orbital of the free chlorine atom is reported as an example, using one Slater orbital only (curve a), a combination of three Slater's orbitals (curve b), and the Hartree–Fock self-consistent function (curve c). It may be noticed that even with three Slater's orbitals the difference with the self-consistent function is still relatively large. However, it may be presumed that wave functions, such as those used in computing the curve b, which contain five parameters (three ζs and two coefficients) are flexible enough to be used to represent the changes of the total wave function (or of the density matrices) which occur when the chlorine atom becomes part of a molecule.

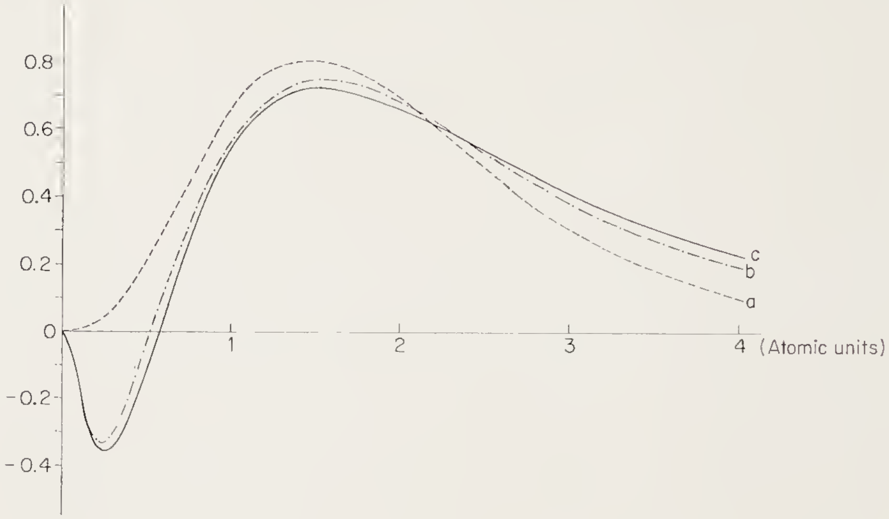

Fig. 1

It must anyway be remembered that in practice there are certain limits to the extension of the number of the variational parameters and that strong complications may arise: for instance the work of Ransil[29] has shown the possibility of finding multiple minima of the energy. This denotes the possible interdependence of the parameters, which would require a limitation of the number of the ζs which may be varied.

As previously said, the other possible way of improving the calculation is to use a set of basic functions of types other than the Slater's functions. Boys[2] and McWeeny[19] suggested the use of Gaussian functions. The advantage of this method lies in the very simple form taken by all necessary integrals, including the three-center and four-center integrals, of electronic repulsion. However, a disadvantage arises from the fact that a higher number of Gaussian functions is necessary to reproduce an atomic orbital with a good accuracy.

A second suggestion has been made by Scrocco and Tomasi[35] and, independently, by M. Geller,[8] to make use of a modified Slater-type atomic orbital.

In this new orbital the zeta contained in the exponent is a function $\zeta = \zeta(r, \theta, \varphi)$ of the three polar coordinates defining the position of the electron with respect to a coordinates system properly oriented and centered on the same nucleus as the orbital.

Atomic orbitals of this type have given encouraging results in the one-electron problem of the H_2^+ molecule. Because of the lack of any experience of many-electron problems it may only be presumed that the number of such functions required to obtain a certain accuracy will be less than the number necessary when using the usual Slater's functions.

However, such a type of function presents the disadvantage of a much greater difficulty in evaluating the integrals.

IV. THE INFLUENCE OF THE INTERACTIONS AMONG THE GROUPS IN A MOLECULE ON THE QUADRUPOLE COUPLING CONSTANT

There is strong experimental evidence that the chemical behavior of polyatomic molecules depends largely on the presence, in the molecule, of particular groups or atoms. This is true to the extent that the chemists classify the compounds according to the functional groups present in their molecules. However, the properties of the various functional groups are not strictly constant, but depend on the molecule to which they belong; it is well known, indeed, that there is a marked influence of the other parts of the molecule.

The study of the reciprocal influence of the various substituents is very interesting for the chemists and it is very likely that an increasing attention will be paid in the future to the theoretical study of this subject.

Examples of the influence of a functional group on the properties of a given atom or group of the molecule are also found in N.Q.R. spectroscopy. In fact, it is known that the quadrupole coupling constant depends on the position of the atom (with a nucleus having a quadrupole moment) in the molecule and depends also on the substitution of one or more groups in the same molecule. This effect is experimentally detected as a change of the resonance frequency of a certain nucleus taking part in a series of similar molecules. For instance, in the $(CH_3)_3CCl(1)$ molecule, the substitution of a CH_3 group by a hydrogen or chlorine atom produces changes of the resonance frequency of the Cl(1) atom, as reported in Fig. 2. Each hydrogen atom which substitutes a methyl group causes a change $\Delta\nu_H = 2.0$ MH and each chlorine atom a change $\Delta\nu_{Cl} = 6.5$ MH.

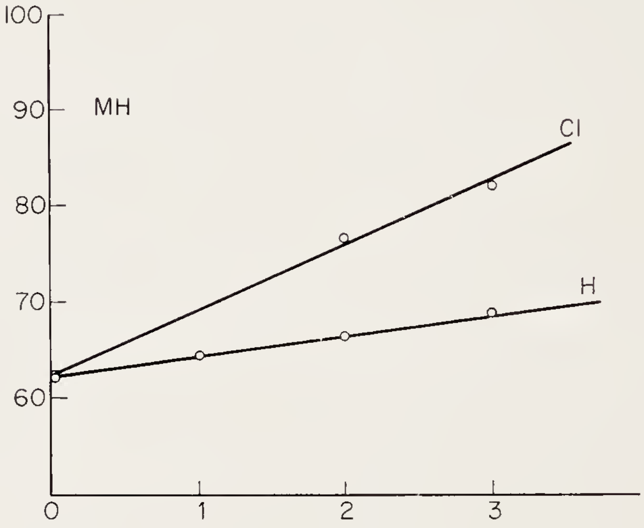

Fig. 2

The chlorobenzenes give another example of the influence of the substituent groups on the quadrupolar frequency of chlorine. By an examination of the experimental data the mean shifts of the frequency of a given chlorine atom of the molecule, caused by another chlorine atom in the *ortho-*, *meta-*, or *para-* position, are easily obtained. These shifts are:

$$\Delta\nu_{ortho} = 2.6 \text{ MH}$$

$$\Delta\nu_{meta} = 0.9 \text{ MH}$$

$$\Delta\nu_{para} = 0.5 \text{ MH}$$

By taking the monochlorobenzene as a reference molecule and using the values given above, it is possible to obtain, by addition. the frequencies given by any chloro-substituted benzene molecule,

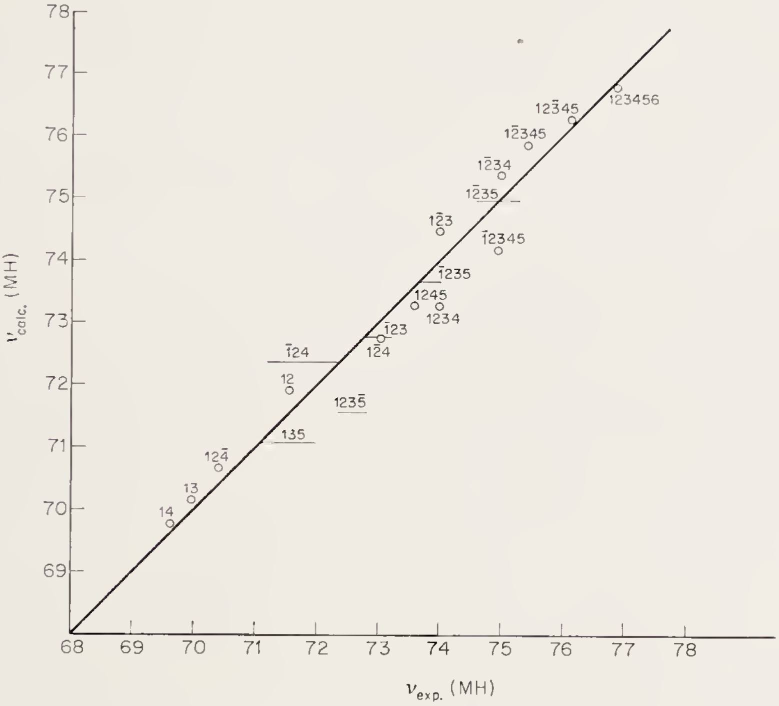

Fig. 3

For instance, in the case of 1,2,3-trichlorobenzene, the frequency of the atom in position 1 is shifted by +2.6 MH with respect to that of monochlorobenzene, owing to the influence of the Cl atom in position 2, and by +0.9 owing to the influence of the chlorine atom in position 3, the total shift being +3.5 MH. The shift of the frequency of the chlorine in position 2 is 5.2 MH, owing to the action of its two *ortho* neighbors (2 × 2.6). Since the monochlorobenzene frequency is 69.24 MH, the two calculated frequencies would be 72.7 and 74.4 respectively, in fairly good agreement with the experimental values 73.04 and 74.0.

Figure 3 is a plot of the frequencies calculated with this method versus their experimental values for all the chlorobenzenes. In some cases more than one frequency is obtained because the chlorine atoms which occupy equivalent positions in the molecule do not occupy equivalent positions in the elementary cell of the crystal lattice. In this case one obtains as many frequencies as there are inequivalent positions present in the lattice. The range of spreading of the experimental frequencies is then indicated in the Figure by a line.

It may be concluded that the shifts of the nuclear quadrupole frequency (of a chlorine atom in a series of similar molecules) may, in a first approximation, be additively attributed to the substituent groups. Each of these groups is characterized by a $\Delta\nu_{g,m,p}$, which is the shift caused by the substituent g in the type of molecule m, in the position p.

A. The Theory of Electron Pairs

The quantum mechanical treatment of the problem (for large molecules) will necessarily introduce some drastic simplifications.

The most apparent simplifications which can be introduced in the treatment of the molecules with covalent bonds consist in neglecting the *direct* contributions to the field gradient of the electrons localized on the atoms far from the quadrupolar nucleus. Such contributions are surely very small and are also partially compensated by the contributions from the respective nuclei, which have the opposite sign.

In this approximation any change of the coupling constant caused by non-adjacent atoms or groups can be considered as an *indirect* effect produced by the deformation that such atoms or groups may induce in that part of the electron cloud which is localized on the quadrupolar atom and on the adjacent bonds.

A tentative application of this idea has been made[34] by using the same molecular wave function which is used in the so-called theory of the "separated electron pairs", developed mainly by Lennard-Jones[13] and, more recently, by Parks and Parr.[27]

The wave function for the 2ν electrons of the molecule is:

$$\Lambda(1,2,\ldots,2\nu) = [\Lambda_A(1,2)\Lambda_B(3,4)\ldots\Lambda_M(2\nu-1,2\nu)] \qquad (29)$$

where the square brackets stand for the antisymmetrization operation by which the complete antisymmetric wave function is obtained from the two-electron functions (pair functions) Λ_I already individually antisymmetric.

Obviously, the Ith pair, described by the generical Λ_I, may be a lone pair or a bond pair. For instance, in the CH_3Cl molecule:

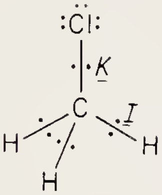

Fig. 4

(considering only the valence shell electrons of the various atoms) there are three electron pairs in the three C—H bonds, another pair in the C—Cl bond and three other lone pairs in the valence shell of chlorine.

The "pair function" Λ_I for a generical bond may, according to Parks and Parr, be written as a linear combination:

$$\Lambda_I = A_{I1}\Phi_{I1} + A_{I2}\Phi_{I2} + A_{I3}\Phi_{I3} \qquad (30)$$

of the following two-electron functions:

$$\begin{aligned} \Phi_{I1} &= \varphi_1(1)\varphi_1(2) \\ \Phi_{I2} &= \frac{1}{\sqrt{2}}[\varphi_1(1)\varphi_2(2) + \varphi_1(2)\varphi_2(1)] \qquad (31) \\ \Phi_{I3} &= \varphi_2(1)\varphi_2(2) \end{aligned}$$

They describe the three singlet configurations of the Ith electron pair obtained from the bonding and antibonding orbitals:

$$\varphi_1 = \frac{\chi_a + \chi_b}{\sqrt{2(1+S)}}; \qquad \varphi_2 = \frac{\chi_a - \chi_b}{\sqrt{2(1-S)}} \qquad (32)$$

$$S = \int \chi_a^\star \chi_b \, d\tau$$

which are expressed as a linear combination of the bond orbitals of the atoms A and B.

The "pair function" for a lone pair is obviously set up by a doubly occupied atomic orbital.

To obtain the complete wave function from the "pair functions", the A_{Ir} coefficients must be known. The calculation may be carried out by successive approximations according to the following scheme: arbitrary values of the A_{Ir} coefficients are first chosen for $\nu - 1$ functions Λ_I and the total energy is minimized with respect to the coefficients of the remaining Λ_K function; the energy is then minimized successively with respect to all pair functions, one at a time. The calculation is repeated until the energies of all electron pairs and the coefficients of all the two-electron functions Λ_I are found.

At this point it is possible to compute, for each bond, a very important quantity: the "polarity parameter" σ_I, which is a measure (in electronic charge units) of the positive electric charge transferred, in the Ith bond, from the atom A_I to the atom B_I. This parameter, defined by the equation:

$$\sigma_I = \frac{\sqrt{2}A_{I2}(A_{I1} + A_{I3})}{\sqrt{1 - S^2}} \tag{33}$$

is closely related to the dipole moment of the Ith bond. Since a change in the electronic population of each orbital results from any charge transfer, the quadrupole coupling constant of an atom participant to the Ith bond is closely dependent on the σ_I parameter.

A detailed study of the problem shows the effect of all the other electron pairs of the molecule on the Kth pair. The (rather intuitive) result is found that the major effect of the substituents is that they induce on the Kth bond a change in the electronegativity of the orbitals χ_a and χ_b and cause therefore a change of the polarity parameter σ_K, relative to the Kth bond. It is also found that this change of σ_K depends, linearly to a first approximation, on the polarity parameters of all the remaining electron pairs of the molecule. This explains how the substitution of some groups of atoms by other different groups causes changes of σ_K which depend on the position where the substitution takes place and are linear with the polarity of the groups and with their number.

A more detailed discussion of this problem is found in ref. 34. Here we only recall some of the results about the quadrupole coupling constant of a chlorine atom contained in an organic polyatomic molecule.

In this problem (in which the perturbation caused by the substituents on the coupling constant of chlorine is calculated) the *direct* contribution of the far charges to the field gradient at the chlorine nucleus is neglected, i.e. only the seven electrons* of the valence shell of chlorine and the valence electron of the carbon atom to which the chlorine is bonded are taken into consideration.

In the "separated electron pairs" theory the eight electrons may be grouped in four distinct pairs as follows:

(1) One pair on the C—Cl σ bond.
(2) One pair on a non-bonding σ orbital.
(3) Two pairs on two non-bonding π orbitals.

The electron pair (1) may be described by a two-electron function such as Eq. (30), built up by a combination of the χ_b orbital (tetrahedral or trigonal) of the carbon atom with a digonal hybrid χ_a of the chlorine atom of the type:

$$\chi_a = \sqrt{\alpha}(3s) + \sqrt{\beta}(3d_{z^2}) + \sqrt{1 - \alpha - \beta}\,(3p_z) \qquad (34)$$

(the z axis has the direction of the C—Cl bond, and α and β are hybridization parameters).

The pair (2) may be described by a second digonal hybrid of the chlorine atom, orthogonal to the first.† Finally, the two remaining pairs may be represented, in a first approximation, by the orbitals $3p_x$ and $3p_y$ of the chlorine atom.

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* The contribution of the inner shell electrons is zero because of the spherical symmetry of their charge distributions, or, at the most, there is a contribution due to their polarization induced by the nuclear quadrupole moment, which is practically constant within a series of similar molecules.

† This hybrid should be orthogonal to the other molecular orbitals, not to the other atomic orbitals of the chlorine; however, since we are not interested, here, in the calculation of the absolute value of the field gradient, but only in its changes from one molecule to a very similar one, this simplification may be reasonable.

The four "pair functions" thus have the expression:

$$\Lambda_1(1, 2) = A_1\Phi_1 + A_2\Phi_2 + A_3\Phi_3$$

$$\Lambda_2(3, 4) = \left[\left(\frac{1-\alpha-\beta}{1-\beta}\right)^{\frac{1}{2}}(3s) - \left(\frac{\alpha}{1-\beta}\right)^{\frac{1}{2}}(3p_z)\right]_3 \left[\left(\frac{1-\alpha-\beta}{1-\beta}\right)^{\frac{1}{2}}(3s) - \left(\frac{\alpha}{1-\beta}\right)^{\frac{1}{2}}(3p_z)\right]_4 \qquad (35)$$

$$\Lambda_3(5, 6) = 3p_x(5)3p_x(6)$$

$$\Lambda_4(7, 8) = 3p_y(7)3p_y(8)$$

With such a simplified description of the eight electrons of the valence shell of the chlorine atom, the expression of the quadrupole coupling constant is as follows:

$$(e^2Qq)_{\text{mol}} = -(e^2Qq_{pz})\left\{\frac{2}{1-\beta} - \left[\frac{A_{K1}^2}{1+S} + \frac{A_{K2}^2}{1-S^2} + \frac{A_{K3}^2}{1-S} + \frac{\sqrt{2}A_{K2}(A_{K1}+A_{K3})}{\sqrt{1-S^2}}\right]\right\}(1-\alpha-\beta) \qquad (36)$$

A simplified form of Eq. (36) which is useful for a semiquantitative interpretation of the results may be obtained by recalling that the last term in square brackets is the polarity parameter of the Kth bond and that the summation:

$$\frac{A_{K1}^2}{1+S} + \frac{A_{K2}^2}{1-S^2} + \frac{A_{K3}^2}{1-S} = \frac{1 - S(A_{K1}^2 - A_{K3}^2)}{1-S^2} \qquad (37)$$

is approximately equal to $1/(1 + S)$ if the bond is not too polarized ($A_{K1}^2 \simeq 1$). Eq. (37) may then take the form:

$$(e^2Qq)_{\text{mol}} = -(e^2Qq_{pz})\left\{\frac{1+2S+\beta}{(1-\beta)(1+S)} - \sigma_K\right\}(1-\alpha-\beta) \qquad (38)$$

which shows explicitly the dependence of the quadrupole coupling constant on the hybridization parameters α and β of the chlorine orbitals and on the polarity parameter σ_K.

Now, in the theory of the "separated electron pairs" as formulated by Parks and Parr it is possible to show that by separating the contributions due to the two nuclei A and B, relative to the

Kth bond, from the remaining contributions, the polarity parameter σ_K can be given the form:

$$\sigma_K = \sigma_K^0 + \frac{1}{(1 - S^2)(H_{22}^K - H_{11}^K)} \sum_{I \neq K} (b_I + c_I \sigma_I) \tag{39}$$

where the first term is the value which the polarity parameter would have in the absence of all the other bonds and electron pairs of the molecule. The second term takes into account the change of σ_K induced by all the Ith electron pairs other than the Kth and it may be shown that: (*a*) $H_{22}^K - H_{11}^K$ is a measure of the difference in the energy of the two configurations described by the two functions Φ_{K1} and Φ_{K2} in Eq. (31); (*b*) each of the terms $(b_I + c_I \sigma_I)$ represents the change in the potential energy difference of the two electrons lying in the χ_{aK} and χ_{bK} orbitals of the Kth bond, such a change being caused by the charge distribution in the Ith bond (or electron pair).

A more detailed analysis shows that, if the Ith and the Kth bonds are far apart, this energy difference is equal to the difference produced by a dipole having $\pm\sigma_I$ charges localized in the centroids of the orbitals χ_{aI} and χ_{bI}.

By substitution of Eq. (39) in Eq. (38) one obtains:

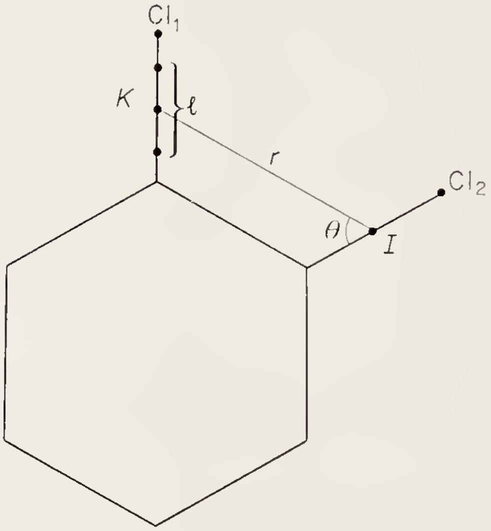
$$(e^2Qq)_{\text{mol}} = (e^2Qq)_{\text{mol}}^0 + \frac{(1 - \alpha - \beta)(e^2Qq_{pz})}{(1 - S^2)(H_{22}^K - H_{11}^K)} \sum_{I \neq K} (b_I + c_I \sigma_I) \tag{40}$$

where the first term is the coupling constant for the case where only the C–Cl bond was present in the molecule and the generic term of the summation yields the expression:

$$\frac{\Delta(e^2Qq)_{\text{mol}}}{(e^2Qq_{pz})} = \frac{(1 - \alpha - \beta)}{(1 - S^2)(H_{22}^K - H_{11}^K)} (b_I + c_I \sigma_I) \tag{41}$$

for the percentage change of the coupling constant due to the Ith electron pair. The right-hand term of Eq. (41) is a function of the nature of the Ith bond and of its location in the molecule.

This last expression may be tested semiquantitatively even when, because of the complexity of the molecule, the molecular wave function is not known. This is, for instance, the case for the dichlorobenzenes (*ortho-*, *meta-*, and *para-*), which have a favourable molecular geometry and may be taken as an example of the possibilities of this method. In this kind of molecule a drastic simplification may be made, which consists in neglecting (or taking as constant) the contributions of the π bonding to the C—Cl bonds and assuming the hybridization of the chlorine orbitals to be the same in the whole group of molecules. Under these assumptions, for each of the electron pairs of the Cl_1 atom and of the C—Cl_1 bond, it is possible to evaluate the quantity $\sum(b_I + c_I\sigma_I)$ as the potential energy change of the two electrons of the C—Cl_1 bond caused by a dipole moment μ localized in the C—Cl_2 bond. The C—Cl_1 bond electrons may be assumed to be localized in the centroids of the two hybrid orbitals χ_C and χ_{Cl_1}.



Assuming reasonable values of the parameters involved in the calculation, the following result is obtained:

$$\Delta(e^2Qq)_{para} : \Delta(e^2Qq)_{meta} : \Delta(e^2Qq)_{ortho} = 0.20 : 0.27 : 1$$

which has to be compared with the experimental result:

$$\Delta\nu_{para} : \Delta\nu_{meta} : \Delta\nu_{ortho} = 0.14 : 0.28 : 1$$

given in the form of the ratios between the frequency changes, with respect to monochlorobenzene, caused by a second chlorine atom which substitutes a hydrogen in the *para-*, *meta-*, or *ortho-*position respectively.

It may be worth noticing that the change of the dipole moment of a certain C—Cl bond induced by another bond may be calculated by Eq. (39). The results are comparable with those already reported for the quadrupole coupling constant.

Considering the strong simplifications which have been made, the result seems to encourage a more accurate analysis of the problem according to the ideas outlined in this chapter. Some improvements will certainly be obtained by eliminating the more drastic assumptions, for instance, by taking into account the possible changes of the hybridization of the chlorine orbitals in going from one molecule to another, and also the possible deformation of the non-bonding orbitals p_x and p_y of the chlorine atom.

B. Future Prospects

In the future work on interactions between groups in a molecule, the McWeeny's theory of the separated electron groups will very probably assume a very important rôle. This theory, which is a particular formulation of the general theory of the density matrix, may also be considered as a generalization of the electron pairs theory.

In McWeeny formulation the N electrons of the molecule are partitioned in a number of partial sets $A, B, C, \ldots, R, \ldots$ each of them containing $N_A, N_B, N_C, \ldots, N_R, \ldots$ electrons $(N_A + N_B + N_C + \ldots = N)$ which are in the states $a, b, c, \ldots r, \ldots$. Each generic group R of electrons, in the state r, is characterized by a group function $\Phi_{R,r}$ (antisymmetric in the coordinates of the N_R electrons) so that the total wave function for a state characterized by the indices a, b, c, etc. may be written, in a first approximation:

$$\Phi_{Aa,Bb,Cc,\ldots} = M\sum_P (-1)^p \Phi_{Aa}(1,2,\ldots,N_A)\Phi_{Bb}(N_A+1,\ldots,N_A+N_B)\ldots \qquad (42)$$

where M is a normalization coefficient, P is a permutation operating only on the electron coordinates of distinct groups and p is its parity.

By using as a basis a set of many-electron functions of this type, it is possible to find a sufficiently approximate molecular wave function by the method of the configurations interaction, which consists in properly selecting a certain number of "states" and then writing down the total wave function as a linear combination of the functions of all the states:

$$\Psi(1,2, \ldots, N) = \sum_{a,b,c,\ldots} c_{a,b,c,\ldots} \Phi_{Aa,Bb,Cc} \tag{43}$$

For a function of this type it is possible to show that the molecular energy may be written as a sum of several terms, each related to a certain degree of approximation:

$$E = E^{(0)} + E^{(1)} + E^{(2)} \tag{44}$$

In Eq. (44) $E^{(0)}$ represents the sum of the energies which the groups would have in the absence of any interaction between them and if each of them were represented only by the configuration of the ground state. The two remaining terms are respectively the polarization and dispersion energies, which depend on the reciprocal interaction of the groups.

The term $E^{(1)}$ is particularly important in the study of the reciprocal influences. It arises from the mixing of the various configurations which are obtained by the excitation of one electron of the generic group R and is closely dependent on the change of the electronic charge distribution in R induced by the other groups. The term $E^{(2)}$, instead, arises from the mixing of the configurations obtained by the simultaneous excitation of two electrons and is then characteristic of the dispersion energy. This last term vanishes very rapidly as the distance between the groups becomes larger and is therefore negligible for well separated electron groups.

The analysis of some interesting details of the McWeeny's theory is outside the limits of this review; however, we believe that this method has all the requirements to be successfully applied to the study of the properties of the more complex molecules and particularly of the reciprocal actions of the substituents. In fact, McWeeny's theory allows a highly complicated molecular problem, which is practically insoluble by the present techniques, to be divided into partial problems which are soluble with sufficient accuracy. The solutions to these partial problems may be successively used as a basis for a further study by the perturbation theory.

Up to now, a sufficient experience in the application of this promising method has not yet been reached; however, there is little doubt that the theory of the separated electron groups is also suitable for the study of the intermolecular forces and of the changes of many molecular properties which accompany the formation of the condensed phases, such as, for instance, the change of the quadrupole coupling constant from the gaseous to the solid state and the effect of the temperature on the same constant in solids.

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COLLISION THEORY OF CHEMICAL REACTION RATES

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I. INTRODUCTION

A formalism for the study of chemical reactions in dilute gases has recently been evolving as a natural extension of what, for many years, kineticists have referred to as the "collision theory." The object of the theory is to analyze the time evolution of gaseous systems which are sufficiently dilute so that any changes which occur can be ascribed to sequences of collisions between pairs of molecules, each collision being a single, discrete event. Chemical reactions occurring under such circumstances are said to be *bimolecular,* and the theory is limited to reactions of this kind. The relevant reactions are then collision-induced dissociations and isomerizations, including the low-pressure limits of reactions which at higher pressure are unimolecular.

The purpose of this article is to present a connected account of this extended collision theory, now that it has reached a point of development in which it is a fairly compact and coherent formalism. It should be understood, however, that the theory is still an object of research interest, for there remains in it a number of open questions, and the validity of some of its basic hypotheses has yet to be fully assessed.

Any collision theory necessarily consists of two essentially different parts, the first being the determination of the cross-sections and transition probabilities for the inelastic molecular collisions which occur, and the second being the statistical part, in which characteristic relaxation and reaction rates are expressed in terms of the assumed known transition probabilities. This article is concerned almost entirely with this second aspect of the theory, in which it proves possible to obtain many explicit results using only very general features of the transition probabilities. Detailed studies of the inelastic collisions themselves, in which the cross-sections are derived from postulated interactions, have not yet led to a consistent and easily summarizable body of results, and are therefore not included in this review.

II. DEFINITIONS AND ASSUMPTIONS

A. Reactant States and Binary Collisions

An unperturbed classical linear oscillator vibrates with a constant energy, while its configuration varies periodically in time. If the state of the oscillator is defined simply by specifying its energy, then one can make only probabilistic statements about the configuration of the oscillator in a given state, that is, one can only say that the probability of finding it within a prescribed range of positions at any instant is proportional to the fraction of its time which is spent in that range when it is in the given state (i.e., when it has the given energy). Likewise, quantum mechanically, if its state is defined by specifying a quantum number, which again amounts to a specification of its constant energy, then once more one can make only probabilistic statements about its configuration when it is in a given state. The WKB theory, furthermore, shows the very close relation between the classical and quantum weighting factors.

Returning to the classical oscillator, imagine that it is subject to occasional collisions. Between collisions the oscillator has a constant energy (i.e., is in a fixed state), but the collision can cause a change in its state. The initial state and the collision parameters (relative energy, impact parameter, etc.) are not in themselves sufficient to determine the change of state that an oscillator will suffer in a collision, because the outcome of the collision depends also on the configuration, or phase, of the oscillator at some suitably defined "beginning" of the collision.[18] On the other hand, if the collisions are random events, and are separated by time intervals which are, on the average, long compared to the period of the oscillator, then these "initial" phases or configurations occur with a perfectly definite probability distribution, as described above. (For example, the phase angle of a linear *harmonic* oscillator will, at the "beginning" of any collision to which the oscillator is subject, be found anywhere in the interval $0,2\pi$ with equal probability.) Under these circumstances, the probability of occurrence of any initial phase is independent of the final phase which resulted from the last collision, i.e., independent of the phase the oscillator had at some suitably defined "end" of the preceding collision. Thus, there is a perfectly definite probability per collision of producing a given change in state (energy) of the oscillator, and this probability depends *only* on the initial state, the final state, and the collision parameters.

These ideas will now be generalized so as to apply to an arbitrary molecule. The motions (rotations and vibrations) of an unperturbed molecule may be described by action and angle variables, the actions being constants of the motion. The state of a molecule is defined by specifying the constant values of independent action variables, equal in number to the number of internal degrees of freedom of the molecule. (This definition is sometimes ambiguous, but the ambiguity is easily resolved; see the discussion of the diatomic molecule below.) These molecules will be said to undergo only binary collisions, and bimolecular reactions, if they are in a gas so dilute that (*1*) the chance of three or more molecules being simultaneously in interaction is negligible, and (*2*) the interval between collisions is long compared to the periods of the molecular rotations and vibrations. That (*2*), as well as (*1*), is an essential part of the definition of a binary collision has also been emphasized by Zwanzig.[23] When these conditions are satisfied, there exists a probability per collision of producing a given change in state of the molecule, this probability depending only on the initial state, the final state, and the collision parameters. The quantum mechanical situation is identical, since defining a state by a complete set of quantum numbers is equivalent to specifying a complete set of constant action variables.

If the states of the molecule are now divided into two classes, i.e., if the molecule's internal action space is divided into two regions, one identified as reactant states and the other as product states, then a bimolecular reaction will consist of collision-induced transitions from states in one class to states in the other. If the state of every identical molecule at any one instant is represented by a point in a common action space, then the assembly of reacting molecules is represented by a cloud of points, and a bimolecular reaction is a *diffusion in action space,** the cloud of representative points being initially concentrated in the reactant region and gradually diffusing into the product region. It will be seen below, however, that this statement is more picturesque than precise, and the lack of precision is connected with the ambiguity in the definition of state already alluded to.

The division of the action space into a reactant region $\mathscr{R}$ and a product region $\mathscr{P}$ may be illustrated by the case of dissociating diatomic molecules, bound molecules being identified as reactant and dissociated molecules as product. A diatomic molecule has three internal degrees of freedom so its state is determined by three independent action variables, which may be conveniently chosen to be the total rotation-vibration energy ε, the angular momentum l of rotations about the center of mass, and the component m_l of the angular momentum in an arbitrarily chosen space-fixed direction $(-l \leqslant m_l \leqslant l)$.

In Fig. 1 is shown the molecule's effective radial potential energy V (true potential plus centrifugal potential) as a function of interatomic distance r, for various angular momenta l. When $l = 0$ the bound states are those of energy between 0 and D, where D is the dissociation energy (classical theory) or dissociation energy plus zero-point energy (quantum theory). There is an angular momentum $l^\star$ above which there are no bound states. When $0 < l < l^\star$, as in curve 2 of Fig. 1, if the molecule is bound then ε lies between the minimum in the curve (point a) and the maximum (point b).

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* A concrete analysis and application of this point of view is given by Wood, J. L., *J. Chem. Phys.* **33**, 1587 (1960).

The reactant region $\mathscr{R}$ in the action space ε, l, m_l is OABD in Fig. 2. It is symmetric with respect to reflection in the plane $m_l = 0$. The line OD is of length D. The line AB, which is parallel to the m_l axis, is of length $2l^\star$ and is situated at the height $\varepsilon^\star$ (see Fig. 1) from the plane $\varepsilon = 0$. The sections OAD and OBD lie in the planes $m_l = l$ and $m_l = -l$, respectively. The upper and lower surfaces, DAB and OAB, of the region $\mathscr{R}$, represent the energy, for varying l, of the points called b and a, respectively, in Fig. 1.

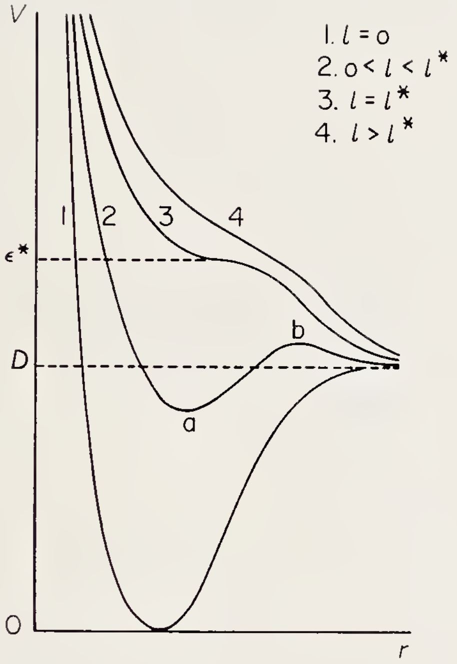

Fig. 1

The region $\mathscr{P}$ of product states is not shown, but it is easily visualized as consisting of all those points that lie above the plane $\varepsilon = D$, but within the dihedral angle formed by the planes $m_l = \pm l$. Thus, *the regions* $\mathscr{R}$ *and* $\mathscr{P}$ *overlap.* The physical reason for this overlap may be seen by referring once more to curve 2 of Fig 1. There are *both* bound *and* dissociated molecules which have angular momenta corresponding to a curve of type 2, and which have energies between D and whatever energy corresponds to point b. Therefore, there are some values of ε, l, m_l which bound and dissociated molecules can have in common. Any such point belonging simultaneously to $\mathscr{R}$ and $\mathscr{P}$ would require a particular designation, such as $(\varepsilon,l,m_l)_{\mathscr{R}}$ or $(\varepsilon,l,m_l)_{\mathscr{P}}$, to identify it unambiguously as a reactant state or a product state. Thus, it is only figurative, but not precise, to say that a state is defined by a set of values of the action variables, and that the classification of states into reactant and product amounts to a separation of the action space into two regions. It is therefore also figurative rather than precise to look upon a bimolecular reaction as a diffusion *across a boundary* from one region of action space to another.

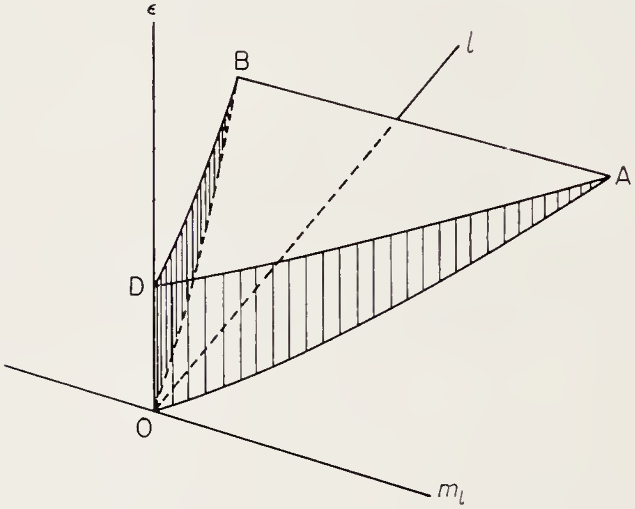

Fig. 2

These geometrical representations allow one to discuss in a simple way possible modes of dissociation which may in reality be quite complex. For example, the transition $(\varepsilon,l,m_l)_{\mathscr{R}} \rightarrow (\varepsilon,l,m_l)_{\mathscr{P}}$ for the case of a point in action space which belongs simultaneously to $\mathscr{R}$ and $\mathscr{P}$ is a perfectly feasible result of a collision; yet it corresponds to a very complicated process in which, during the course of a single collision, the diatomic molecule is first excited and then de-excited in such a way as to carry it over a potential energy maximum such as point b of Fig. 1. As another example, consideration of the boundary surface DAB of the region $\mathscr{R}$ in Fig. 2 shows the possibility of dissociation by rotational de-excitation,* and, indeed, the possibility of dissociation resulting from a net *decrease* in the total energy of the molecule. Here again, however, the actual collision processes are quite complicated, involving simultaneous rotational de-excitation and vibrational excitation.

No important change of viewpoint is required for the quantum mechanical description. For example, all the bound states are still to be found within OABD of Fig. 2, but now it is only discrete points within this region which correspond to states, rather than the entire volume. There are no states of energy greater than D which are bound in the strict quantum mechanical sense, but since barrier penetration is usually quite negligible, the WKB theory can be used to find those states which, for any l in the range $0 < l < l^\star$, have energy greater than D but less than that of the effective potential energy maximum, and which in practice are to be counted among the bound states. The regions $\mathscr{R}$ and $\mathscr{P}$ still overlap, exactly as in the classical case, and for the same reason.

B. Transition Probabilities and Detailed Balance

The discussion is greatly simplified if one of the colliding molecules has a fixed internal state, unchangeable by collision; it might, for example, be an inert gas atom, in a system at a temperature low enough for electronic excitation to be rare. Without such a condition the basic relaxation and rate equations, which will be introduced in Section III, could not be linear. This simplification will be adopted here, so that the reactive molecules, symbolized by A, are to be thought of as dispersed sufficiently dilutely in a gas of inert molecules, symbolized by X, so that A–A collisions may be ignored and only A–X collisions need be considered. It is assumed further that the diluent gas X is itself so dilute that the interval between collisions suffered by any one A molecule is long enough to satisfy the conditions given in Section

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* That such a mechanism may be of importance in the reaction has been suggested by Bauer, S. H., Abstr. No. 20, Div. Phys. Chem., 133rd meeting ACS, San Francisco (April, 1958).

II-A for the collisions to be binary. The reactions undergone by A will then be truly bimolecular, and of the type

$$X + A \rightarrow X + \text{products} \tag{1}$$

The binary collision conditions are *not* satisfied when X forms with A a long-lived complex which is itself capable of undergoing collisions, so reactions of this kind are formally excluded. Nevertheless, if X–A complexes are formed almost instantaneously then the theory is again applicable, the complexes XA simply playing the part of the molecules A in Eq. (1).

Let the state of a molecule A be denoted by a single symbol, say x, so that x stands for a point in the molecule's internal action space, except that it may have to be a specially labeled point if, as in the illustration discussed earlier, one and the same set of values of the action variables can characterize more than one state. Further, let dx be an element of volume in the action space. It was seen in Section II-A that when the binary collision conditions are satisfied there is a probability per collision for the occurrence of any given change in state, this probability depending only on the initial state, the final state, and the collision parameters. Thus, let

$$q(x,y;p)dy$$

be the probability that an A molecule initially in state x will make a transition to a state y in the region dy when it suffers a collision with X in which the collision parameters are symbolized by p. In three-dimensional collisions p represents five quantities, which may be chosen to be the initial kinetic energy of relative motion E, the impact parameter b (i.e., the quantity that would be the distance of closest approach of the centers of mass of A and X if there were no interaction between them), and three appropriately defined angles θ, ϕ, ψ $(0 \leqslant \theta \leqslant \pi,\ 0 \leqslant \phi \leqslant 2\pi,\ 0 \leqslant \psi \leqslant 2\pi)$ to complete the specification of the initial trajectory of relative motion. In two-dimensional collisions p represents three quantities, which may be chosen to be E, b, and an angle ψ $(0 \leqslant \psi \leqslant 2\pi)$, and in one-dimensional collisions p represents one quantity, which may be chosen to be E.

These transition probabilities may be expressed alternatively as total cross-sections, although these contain somewhat less detail than the probabilities themselves, since for given initial and final states of the molecule they depend only on E but are independent of any of the other collision parameters contained in p. If

$$\sigma(x,y\,;E)dy$$

is the cross-section for the process in which the molecule makes a transition from state x to a state y in dy, owing to a collision characterized by initial relative translational energy E, then in three-, two-, and one-dimensional systems, respectively,

$$\sigma(x,y\,;E) = (1/4\pi)\int_0^\infty \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} q(x,y\,;E,b,\theta,\phi,\psi)b \sin\theta \, d\theta d\phi d\psi db$$

$$\sigma(x,y\,;E) = (1/\pi)\int_0^\infty \int_0^{2\pi} q(x,y\,;E,b,\psi)d\psi db$$

$$\sigma(x,y\,;E) = q(x,y\,;E) \tag{2}$$

The three-dimensional cross-section is an effective area, the two-dimensional cross-section is an effective length, and the one-dimensional cross-section is a dimensionless quantity which is identical with the transition probability per collision, $q(x,y\,;p)dy$.

In the analogous quantum theory an internal state of the molecule is defined by a set of quantum numbers, which can be represented by a single symbol such as i or j. Then the probability that a molecule initially in state i will make a transition to state j when it suffers a collision characterized by appropriately defined parameters p can be symbolized by $q_{ij}(p)$, and cross sections $\sigma_{ij}(E)$ exactly analogous to those of Eqs. (2) are familiar quantities in quantum mechanical scattering theory.

A very general treatment of the collision theory would proceed from here to follow the time evolution of the states of relative translational motion while simultaneously following the changes in population of the internal molecular states.[13] However, the theory is very greatly simplified by making the approximation that, relative to the time required for significant changes to occur in the populations of internal molecular states, *translational* *relaxation is instantaneous,** so that the relative translational motion of A and X is at all times determined by the velocity distribution appropriate to a system at equilibrium at a single fixed temperature T. Implied here is also the assumption that the system is in a thermostat which is instantaneously effective, or, equivalently, that the diluent gas X is present in such large excess as to have an effectively infinite heat capacity. With these assumptions it follows that if

$$z(p)dp$$

is the number of collisions per unit time suffered by each A molecule, in which the collision parameters p lie in the range dp, then $z(p)$ is independent of the time. Indeed, from classical kinetic theory, taking dp to be $dEdbd\theta d\phi d\psi$, $dEdbd\psi$, or dE for three-, two-, or one-dimensional systems, respectively,

$$\begin{aligned} z &= 2c\mu^{-\frac{1}{2}}(2\pi kT)^{-\frac{3}{2}}E \exp(-E/kT) b \sin\theta \\ z &= c(2/\mu)^{\frac{1}{2}}(\pi kT)^{-1}E^{\frac{1}{2}} \exp(-E/kT) \\ z &= c(2/\pi\mu kT)^{\frac{1}{2}} \exp(-E/kT) \qquad (3) \end{aligned}$$

where k is Boltzmann's constant, μ is the reduced mass of A–X, and c is the concentration of X, i.e., the number of molecules of X per unit volume, per unit area or per unit length.

If Z is the total number of collisions per unit time suffered by each A molecule, then $z(p)dp/Z$ is the probability that any collision suffered by an A molecule will be one in which the collision parameters lie in the range dp about p. From this it follows that $Z^{-1}q(x,y;p)z(p)dydp$, when integrated over all p, is the probability that a molecule in state x, if it suffers a collision of unspecified type, will make a transition to a state y within dy. On the other hand, $Z\Delta t$ is the probability that a molecule will suffer a collision within an infinitesimal time interval Δt. Thus, the quantity $k(x,y)$ defined by

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* This condition, coupled with the earlier ones, now guarantees the linearity of the basic relaxation and rate equations.

It is of interest that, in a certain sense, this assumption is the opposite of that made by Prigogine, I. and Xhrouet, E., *Physica* **15,** 913 (1949); Prigogine, I. and Mahieu, M., *Physica* **16,** 51 (1950); Prigogine, I., *J. Phys. and Coll. Chem.* **55,** 765 (1951); and Takayanagi, K., *Prog. Theor. Phys.* **6,** 486 (1951); who ignore the internal molecular states but treat explicitly the effect on the reaction of the translational relaxation process. Thus, they estimate the effect on the reaction rate constant of a non-Maxwellian translational distribution, just as in the present article the effect of a non-equilibrium distribution of molecules among internal states is studied. Indeed, formally, the two theories can be developed in such a way as to be exact analogs of each other, though they differ in their physical meaning.

$$k(x,y) = \int\limits_{\text{All } p} q(x,y;p)z(p)dp \tag{4}$$

is such that $k(x,y)dy$ is the *transition probability per unit time*, that is, $k(x,y)$ is the kernel of a relaxation equation such as Eq. (11) below.

The transition kernel $k(x,y)$ may be expressed in terms of the cross sections by combining Eqs. (2), (3), and (4). Thus,

$$k(x,y) = \nu_s c(kT/\mu)^{\frac{1}{2}} \int_0^\infty \sigma(x,y;E)(E/kT)^{(s-1)/2} \exp(-E/kT)dE/kT \tag{5}$$

where s is the dimensionality of the system, and $\nu_3 = 2(2/\pi)^{\frac{1}{2}}$, $\nu_2 = 2^{\frac{1}{2}}$, $\nu_1 = (2/\pi)^{\frac{1}{2}}$.

In the quantum formalism a transition probability per unit time k_{ij} is related to the transition probability per collision $q_{ij}(p)$ by the exact analog of Eq. (4), or to the cross-section $\sigma_{ij}(E)$ by the exact analog of Eq. (5).

Throughout this article it will be assumed that, at equilibrium, in any given time interval, exactly as many molecules make transitions from the range of states dx about x to the range of states dy about y as make transitions from the range dy to the range dx. Therefore, if

$$f(x)dx$$

is proportional to the fraction of all A molecules which would have states x in the range dx if the system were in equilibrium at temperature T (i.e., if f is the Boltzmann distribution) then

$$f(x)k(x,y) = f(y)k(y,x) \tag{6}$$

which is the condition of *detailed balance* that the transition probability per unit time must satisfy. The analogous condition in the quantum formalism is $f_i k_{ij} = f_j k_{ji}$. The condition may be considered to arise from Eq. (4) or (5) and to be ultimately traceable to the appropriate symmetries between initial and final states shown by the transition probabilities per collision, or, equivalently, by the cross-sections.*

C. Collision Number and Completeness

The quantity symbolized by $q(x,y;p)dy$ is the probability that a molecule initially in state x will make a transition to some state in the region dy in the neighborhood of y as the result of a collision characterized by parameters p. Therefore, identically for any x and p,

$$\int_{\text{All states } y} q(x,y;p)dy = 1 \tag{7}$$

which expresses the *completeness* of the transition probability per collision. Then from Eqs. (4) and (7) there follows a corresponding condition of completeness for the transition kernel $k(x,y)$: For any x,

$$\int_{\text{All states } y} k(x,y)dy = \int_{\text{All } p} z(p)dp = Z \tag{8}$$

where Z, the collision number, is again the total number of collisions per unit time suffered by each A molecule. Likewise, in the quantum formalism, for any i

$$\sum_j k_{ij} = Z \tag{9}$$

provided the summation is over *all* states j, *including* state i, just as the state x is included in the range of integration over y in Eqs. (7) and (8). The reason for having to include the initial state in the range of summation or integration over final states is that the completeness conditions arise from considering *all* the possible results of a collision, and *no transition* is one such possible result.

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* Though in the form in which it is stated here it is not a principle of completely general validity, detailed balance has nevertheless been found to hold in all models which have yet been applied to the study of chemical reaction rates. The question is not a very important one here, however, for the essential results of the theory do not depend on detailed balance; it is just that without it one loses the convenience of working with the *symmetric* kernel S introduced in Eq. (14) below.

The author is indebted to Profs. J. de Boer and N. G. van Kampen for having pointed out to him the restricted validity of the principle.

In one-dimensional systems the collision number Z is finite and, from Eqs. (3) and (8), it is just $c(2kT/\pi\mu)^{\frac{1}{2}}$. In two- and three-dimensional systems, however, the integration over all p in Eq. (8) includes a divergent integral over the impact parameter b, so $Z = \infty$, expressing the fact that if every passage of an X molecule past an A molecule is counted as a collision, however great the impact parameter, then necessarily each A suffers an infinite number of collisions per unit time.

One of the consequences of the divergence of the collision number in two- and three-dimensional systems is, according to Eq. (8), that the integral over all states y of $k(x,y)$ is infinite. There is a diagonal singularity in $k(x,y)$, that is, a singularity at $y = x$, sufficiently strong to cause the divergence of the integral. The reason for this is that if two states x and y are very close together, then even a very distant collision produces a strong enough interaction to effect the transition from the one state to the other; furthermore, in two and three dimensions, increasingly large numbers of collisions occur with impact parameter up to some increasingly large limit; so that in unit time there occurs an infinite number of collisions capable of producing a transition between infinitesimally separated states x,y. Thus, in a system of dimensionality greater than one, $k(x,y)$ is necessarily infinite when $y = x$. The singularity is due to the counting of very distant collisions, and it is the same phenomenon as the divergence of the (classical) elastic scattering cross-section.

The detailed nature of the diagonal singularity can be estimated as follows. Suppose the molecule has h internal degrees of freedom, so that the space of states (action space) is h dimensional Let δ be the infinitesimal "distance" in action space separating two nearby states x and y, and let ε be the energy of a molecule in state x. Then the magnitude of the difference in energy between a molecule in state x and a molecule in state y is

$$|\text{grad } \varepsilon|\delta$$

where "grad" is the gradient operator in action space. If now one supposes that a collision can be effective in producing a change of state when the interaction energy in the collision is of the order of magnitude of the difference in energy of the two molecular states, and if the interaction energy between A and X decreases with the nth power of the distance between them when this distance is large, it follows that collisions of all impact parameters up to those of the order of magnitude of $\delta^{-1/n}$ can be effective in producing the contemplated infinitesimal change in state. But when the system is of dimensionality s (with $s = 2$ or 3) the number of collisions with impact parameter less than this which each A suffers in unit time is of the order of magnitude of $\delta^{-(s-1)/n}$. If in Eq. (8) one excludes from the range of y those states within a "distance" δ of state x, and correspondingly excludes from Z those collisions which occur with impact parameters greater than $\delta^{-(s-1)/n}$, and if one supposes that

$$k(x,y) \sim \delta^{-N}$$

when y is close to x, it follows that

$$\int_{\delta}^{\infty} r^{-N} r^{h-1}\, dr \sim \delta^{-(s-1)/n}$$

that is, that $N = h + (s - 1)/n$. Thus, the diagonal singularity in $k(x,y)$ is of the form

$$k(x,y) \sim \delta^{-h-(s-1)/n} \qquad (s = 2,\ 3) \tag{10}$$

There has always been closely associated with the collision theory of chemical reactions the notion that there is a more or less sharply definable range of interaction, call it $b^\star$, such that if the true interaction between A and X were replaced by a fictitious interaction which vanished identically when the distance between the centers of mass of A and X exceeded $b^\star$, but was otherwise identical to the true interaction, then the course of the chemical reaction would be only negligibly perturbed. Such a replacement would have the effect of allowing one to ignore all collisions of impact parameter greater than $b^\star$, and it would therefore allow one to define a physically meaningful collision number Z (as a function of $b^\star$) which is finite whatever the dimensionality of the system. Indeed, some such notion is already implicit in the language used to state the binary collision conditions in Section II-A, where it is required that the interval between collisions be long compared to the periods of the molecular rotations and vibrations; if *all* collisions were included this interval would be zero and the condition would never be satisfied.

The idea of such a cutoff can be formally incorporated in the theory. Let the true interaction be replaced by the fictitious interaction described above, with an arbitrarily chosen $b^\star$ that is a fixed length, independent of the internal state of A. The

$q(x,y;p)$ appropriate to this auxiliary model still satisfies the completeness relation of Eq. (7). The corresponding $k(x,y)$ for the auxiliary model is to be determined from this $q(x,y;p)$ by Eq. (4), but with the range of integration restricted to $b \leqslant b^\star$. Then combining these two relations, just as before, there results Eq. (8), but with the range of integration over p now restricted to $b \leqslant b^\star$, and with Z now the total number of collisions per unit time suffered by each A molecule in which the impact parameter b does not exceed $b^\star$. The new quantities $q(x,y;p)$, $k(x,y)$, and Z defined in this way all depend parametrically on $b^\star$. The statements that $k(x,y)dy$ is the transition probability per unit time, so that $k(x,y)$ is the kernel of a relaxation equation, and that $k(x,y)$ satisfies detailed balance, would apply with equal validity to the $k(x,y)$ of the auxiliary model and to the true $k(x,y)$.

One can now proceed to interpret the later results (concerning relaxation times, reaction rates, etc.) from either of two points of view. The quantity $b^\star$ can be imagined fixed at some value corresponding to a true physical distance beyond which interaction between A and X is negligible; the characteristic times, etc., which follow from the theory will then be approximations, the accuracy of which will depend on how sharply definable such a $b^\star$ really is. The alternative point of view is to note that any physically meaningful quantity that depends parametrically on $b^\star$ will necessarily approach a finite limit as $b^\star \rightarrow \infty$, and that the true value of the quantity is this limiting value. For example, characteristic times associated with the reaction will later be identified with $(Z - \mu_i)^{-1}$, where the μ_i are the eigenvalues of a kernel which is closely related to $k(x,y)$. Then both Z and μ_i depend parametrically on $b^\star$, and one can take the true characteristic time to be

$$\lim_{b^\star \rightarrow \infty} (Z - \mu_i)^{-1}$$

there being, presumably, a finite limit. With the understanding that one or the other of these points of view has been adopted, the formalism will be developed as though $k(x,y)$ satisfies the completeness condition of Eq. (8) with a constant collision number Z which is independent of the molecular state x, and which is finite whatever the dimensionality of the system.

III. RELAXATION EQUATION AND RATE EQUATION

A. Relaxation Equation and Its Formal Solution

As the molecules A undergo collisions with X the total number of A molecules in any one internal state gradually changes, and the distribution of molecules among internal states gradually approaches a Boltzmann distribution. This process of approach to the equilibrium distribution is called relaxation. In the example of diatomic molecules A described in Section II-A, if all the states, both bound and dissociated, took part in such a process, there would ultimately be established complete chemical and thermal equilibrium, every state having its equilibrium population. As it happens, this particular relaxation process cannot be treated by the present theory, because molecules in dissociated states necessarily fail to satisfy the binary collision conditions in their collisions with X. Suppose, however, that the interaction of a bound molecule with X were of a very peculiar character, such as to lead to vanishing probability for any transition from a state in $\mathscr{R}$ to a state in $\mathscr{P}$. Then the transition probability would be complete in the region $\mathscr{R}$, that is, the integrations over states in Eqs. (7) and (8) could be restricted to states in $\mathscr{R}$, and one could discuss the relaxation of the bound states among each other. The relaxation of reactant states among each other is actually a very instructive reference system for the discussion of the chemical reaction $\mathscr{R} \rightarrow \mathscr{P}$, since, as will be seen later, there are numerous occasions on which it is convenient to look upon a chemical reaction as being merely a slight perturbation of a relaxation process in $\mathscr{R}$, the perturbation consisting of a slow leak from $\mathscr{R}$ to $\mathscr{P}$.

This section is mainly concerned with the formal theory of relaxation processes, so it will be supposed that the molecules A undergo transitions among a set of states due to collisions with X, that the binary collision conditions are satisfied, and that over this set of states the transition probability is complete and satisfies detailed balance. An integral written without indicated limits will be understood to extend over all the states in question.

Let $c(x,t)dx$ be the total number (*or* the fraction, *or* the number per unit volume) of A molecules which at time t have internal states x in the range dx. Then, since $k(x,y)dy$ is the transition probability per unit time,

$$\partial c(x,t)/\partial t = \int [k(y,x)c(y,t) - k(x,y)c(x,t)]dy \qquad (11)$$

In the quantum formalism the analogous equation is

$$dc_i(t)/dt = \sum_j [k_{ji}c_j(t) - k_{ij}c_i(t)] \qquad (12)$$

which makes it clear that these *relaxation equations* are mathematically equivalent to what a kineticist would consider the rate equations for a set of coupled first-order reactions (i.e., first order in the c's; each k is proportional to the constant concentration of X molecules so the processes are bimolecular). The A molecules in a particular state are analogous to a distinct chemical species and the transition probabilities are analogous to rate constants.

These being the fundamental equations of the theory, they must remain meaningful even when the collision number is infinite, that is, even when the kernel $k(x,y)$ or the matrix k_{ij} has a diagonal singularity strong enough to cause the divergence of the integral in Eq. (8) or the sum in Eq. (9). That this is the case with the quantum form in Eq. (12) is immediately obvious, since the term $j = i$ can be omitted at will from the summation, so it is a matter of complete indifference whether k_{ii} is infinite or finite. The integral in the classical Eq. (11) can, because of detailed balance (Eq. (6)), be written

$$\int k(x,y)[f(x)c(y,t)/f(y) - c(x,t)]dy$$

If the function of y in square brackets is expanded in a power series about x, and if one notes Eq. (10), it is seen that the contribution to the integral which comes from the neighborhood of the singularity is essentially

$$\int_0^\delta r^{-h-(s-1)/n+1}\, r^{h-1} dr$$

so that the integral in Eq. (11) converges so long as $n > s - 1$, that is, so long as the interaction energy between A and X at large separations falls off faster than the inverse square of the distance between them, or faster than the inverse of the distance between them, in three- and two-dimensional systems, respectively. As already noted, however, the formal development can proceed with the assumption of a finite collision number, and these remarks will then be irrelevant.

A quite different point will also be noted here. One can make the approximation that the transition probability $k(x,y)$ is insignificant when the states x,y are appreciably separated in action space, so that the only transitions which need be considered are those which, in action space, are represented by very small steps. It is then possible to derive from Eq. (11), or from Eq. (13) or (21) below, an approximating partial differential equation for $c(x,t)$ which is a diffusion equation of the Fokker–Planck, Kramers, Smoluchowski type.[5,17] Although this makes the interpretation of chemical reaction and relaxation as a diffusion in action space more graphic, it seems to lead neither to greater insight nor to increased simplicity, so the details of the approximation will not be given here.

For the remainder of this article the language used will be that appropriate to the classical theory, but the methods and results are identical to those of the quantum theory, and one can transcribe at will from a continuum formulation, in which the transition probability is a kernel, to a discrete formulation, in which the transition probability is a matrix.

The relaxation equation, Eq. (11), can be rewritten as

$$\partial c(x,t)/\partial t = \int k(y,x)c(y,t)dy - Zc(x,t) \tag{13}$$

using the completeness condition of Eq. (8). Because of the condition of detailed balance in Eq. (6), the kernel

$$S(x,y) = S(y,x) = [f(x)/f(y)]^{\frac{1}{2}}k(x,y) \tag{14}$$

is symmetric. Let its eigenfunctions and eigenvalues be $\phi_i(x)$ and μ_i $(i = 0, 1, 2, \ldots)$ so that

$$\int S(x,y)\phi_i(y)dy = \mu_i\phi_i(x) \tag{15}$$

Then the formal solution of Eq. (13) with an arbitrarily prescribed $c(x,0)$ is

$$c(x,t) = f(x)^{\frac{1}{2}} \sum_{i=0}^{\infty} h_i\phi_i(x) \exp\left[-(Z - \mu_i)t\right] \tag{16}$$

where

$$h_i = \int f(x)^{-\frac{1}{2}}c(x,0)\phi_i(x)dx \Big/ \int \phi_i^2(x)dx \tag{17}$$

From the physical interpretation of Eq. (16) it is clear that the eigenvalues will be capable of being ordered in such a way that

$$Z = \mu_0 > \mu_1 > \mu_2 > \ldots \tag{18}$$

The largest eigenvalue must be Z, so that the first term in Eq. (16) will be the equilibrium population $c(x,\infty)$, while the remaining terms are transients. The equilibrium population must be proportional to the Boltzmann distribution $f(x)$, while from Eq. (16) it is seen to be proportional to $f(x)^{\frac{1}{2}}\phi_0(x)$. Thus, for this interpretation to be consistent it is necessary that

$$\phi_0(x) = \text{const}\, f(x)^{\frac{1}{2}} \tag{19}$$

that is, that the square root of the Boltzmann distribution be the eigenfunction belonging to the largest eigenvalue, Z. But that $f(x)^{\frac{1}{2}}$ is indeed an eigenfunction of $S(x,y)$, with eigenvalue Z, follows immediately from the completeness condition of Eq. (8). This is entirely equivalent to the appearance of a zero eigenvalue, as an expression of conservation of matter, in the conventional solution of the matrix Eq. (12) with the term $j = i$ omitted from the summation.

The characteristic times

$$\tau_i = (Z - \mu_i)^{-1} \qquad (i = 1, 2, \ldots) \tag{20}$$

are the *relaxation times*. The largest is τ_1, according to the ordering of Eq. (18), and it is this one which determines the rate of approach to equilibrium in the last stages of the relaxation process. It is very important to note that the characteristic times do not in any way depend on the initial distribution $c(x,0)$.

B. Rate Equation and Its Formal Solution

In experimental chemical kinetics one often tries to separate a reaction from its inverse, in order to study each one apart from the other. This can be accomplished in principle by the instantaneous removal from the reaction system of all molecules A in product states. It is usually assumed that in practice this condition may be realized by starting with all molecules in reactant states and then observing the system only for times sufficiently short so that the concentration of product molecules remains too small for the inverse reaction to occur at a significant rate. This is most likely to be successful in a dissociation reaction, for then the inverse reaction, which is a recombination, is of higher molecularity and will remain negligible for a relatively very long time.

Suppose that, by instantaneous removal of products or by any other means, a condition has been achieved in which a molecule appearing in a reactant state can only have come from some other reactant state, while a molecule leaving a reactant state can go either to another reactant state or to a product state. Then if x is any reactant state, Eq. (11) is to be replaced by

$$\partial c(x,t)/\partial t = \int_{\mathscr{R}} k(y,x)c(y,t)dy - c(x,t) \int_{\mathscr{R}+\mathscr{P}} k(x,y)dy$$

or, since the transition probability is complete over the full range of states $\mathscr{R} + \mathscr{P}$,

$$\partial c(x,t)/\partial t = \int_{\mathscr{R}} k(y,x)c(y,t)dy - Zc(x,t) \qquad (x \text{ in } \mathscr{R}) \qquad (21)$$

In these expressions $\mathscr{R}$ and $\mathscr{P}$ are to be taken as representing the full ranges of reactant states and of product states. They can be precisely identified with the geometric regions $\mathscr{R}$ and $\mathscr{P}$ discussed in Section II-A only if the latter do not overlap.

It is significant that in Eq. (21) the initial states in the transition kernel are always reactant states, never product states. It has already been noted that in a dissociation reaction, molecules A in product states (that is, dissociated molecules) necessarily fail to satisfy the binary collision conditions in their collisions with X, but this does not affect the validity of Eq. (21). On the other hand, it means that only in the case of an isomerization is the present theory applicable simultaneously to a reaction and to its inverse.

Equation (21) is called the *rate equation*, and it differs from the relaxation equation, Eq. (13), in that the transition probability is presumed complete over the region of integration in Eq. (13) while it is not complete over the range $\mathscr{R}$ in Eq. (21). Put less abstractly, in the process described by Eq. (13) a molecule must make a transition to states in the range of integration, while in the process described by Eq. (21) a reactant molecule may make a transition to states outside $\mathscr{R}$, i.e., it may form a product molecule and then be removed from the system. Thus, if x is any reactant state, one must now expect $c(x,\infty)$ to be zero, rather than a non-zero equilibrium population as in Section III-A.

A symmetrized transition kernel can still be defined in terms of $k(x,y)$ and the Boltzmann distribution according to Eq. (14). Now let $\phi_i(x)$ and μ_i be its eigenfunctions and eigenvalues in the region $\mathscr{R}$, so that Eq. (15) holds with the integral extended over $\mathscr{R}$. Then the formal solution of Eq. (21) with an arbitrarily prescribed $c(x,0)$ is still given by Eqs. (16) and (17), provided that in Eq. (17) the integrals are extended over $\mathscr{R}$. The significant differences between the solutions are that in the analog of Eq. (18) the equality is now to be replaced by an inequality:

$$Z > \mu_0 > \mu_1 > \mu_2 > \ldots \tag{22}$$

so that $c(x,\infty) = 0$; and that Eq. (19) no longer holds. Since the transition probability is not complete in $\mathscr{R}$ it is no longer true that the largest eigenvalue is Z and it is no longer true that the corresponding eigenfunction $\phi_0(x)$ is proportional to $f(x)^{\frac{1}{2}}$.

The characteristic times τ_i ($i = 1, 2, \ldots$) given by Eq. (20) are still called relaxation times. The additional quantity $(Z - \mu_0)$ is now also of importance, and it will later (Section IV-A) be identified with the rate constant.

In Section III-A it was pointed out that as a convenient reference for the discussion of a chemical reaction one could consider the relaxation of an artificially constructed system in which the transition probability is complete in $\mathscr{R}$. In the reference system all transitions occur within $\mathscr{R}$, and the reaction system is a perturbed form of the reference system, the perturbation consisting of a small but non-vanishing probability of transition from reactant states to product states. Then if the reaction is slow, that is, if the perturbation is small, the quantity $(Z - \mu_0)$ for the reaction system will be small (being zero in the reference system), and the relaxation times τ_i in the reaction system will be only slightly different from the relaxation times in the reference system. The equality $\phi_0(x) = f(x)^{\frac{1}{2}}$, which is exact for the pure relaxation process, would remain a close approximation when the relaxation is accompanied by slow reaction, and $f(x)^{\frac{1}{2}}$ would therefore be a very convenient choice of trial function for $\phi_0(x)$ in variational calculations. Indeed, the full apparatus of perturbation and variation techniques is applicable here.

This section has been concerned with the solution of Eq. (21), which is the equation appropriate for the case in which product molecules are instantaneously removed from the system. Just how accurately, and under just what circumstances, the idealization of instantaneous removal of products applies to chemical reactions under real experimental conditions, is still a very serious open question.*

IV. REACTION RATE

A. Rate Constant and Relaxation Times

The time evolution of a reaction system subject to instantaneous removal of reaction products is given by Eq. (16), with $\phi_i(x)$ and μ_i the eigenfunctions and eigenvalues of $S(x,y)$ in $\mathscr{R}$. According to Eq. (22) the smallest of the positive decay constants $(Z - \mu_i)$ is $(Z - \mu_0)$, so after sufficiently long times

$$c(x,t) = h_0 f(x)^{\frac{1}{2}}\phi_0(x) \exp\left[-(Z - \mu_0)t\right]$$

If the number of reactant molecules present at time t is $C(t)$, then

$$C(t) = \int_{\mathscr{R}} c(x,t)dx \tag{23}$$

so after sufficiently long times

$$-dC(t)/dt = (Z - \mu_0)C(t) \tag{24}$$

Thus, after a time long enough for the further evolution of the system to be determined by the smallest decay constant, the system will be characterized by a *rate constant* κ given by

$$\kappa = Z - \mu_0 \tag{25}$$

For this to be true the system must first evolve for a time long compared to $(Z - \mu_1)^{-1}$, that is, long compared to the longest relaxation time.

Throughout this article *rate constant* will mean the first-order rate constant associated with Eq. (1), that is, the conventional second-order rate constant multiplied by the constant concentration of X molecules.

Rate constants are of the order of magnitude of $Z \exp(-\varepsilon_0/kT)$, ε_0 being the activation energy, whereas relaxation times are of the order of magnitude of Z^{-1}. Ordinarily $\varepsilon_0 \gg kT$; indeed, it is $\exp(-\varepsilon_0/kT)$ which is the most convenient quantity to choose as a perturbation parameter when treating the reaction system as a perturbation of the reference relaxation system, and to say that the perturbation is expected to be small when the reaction is slow is equivalent to saying that $(Z - \mu_0)$ differs only very slightly from its unperturbed value of zero when $\varepsilon_0 \gg kT$. Under these circumstances the characteristic reaction time κ^{-1}, that is, the time during which a significant fraction of the reactant molecules disappears, is much greater than the relaxation time, since $Z^{-1} \exp(\varepsilon_0/kT) \gg Z^{-1}$. Thus, relative to the reaction time, the relaxation time passes almost instantaneously, so during its entire course the reaction is characterized by the single, well-defined rate constant κ.

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* Some consequences of this idealization have been vigorously criticized by Rice, O. K., *J. Phys. Chem.* **65**, 1972 (1961).

At temperatures so high that $\exp(-\varepsilon_0/kT)$ is comparable to unity it is no longer true that the evolution of the system is effectively characterized by a single time constant, but rather, during most of its course, a large number of terms in Eq. (16), containing many time constants, contribute significantly to the measurable changes in the system. This can be the case even when $\exp(-\varepsilon_0/kT)$ still appears rather small, because it is not unusual for κ to be of the order of magnitude of $100Z \exp(-\varepsilon_0/kT)$, nor is it unusual for relaxation times to be of the order of magnitude of $1000Z^{-1}$. Significant coupling between the processes of dissociation and vibrational relaxation has been found to occur in oxygen at temperatures above 8000 °K,[2] and under these circumstances $\exp(-\varepsilon_0/kT) \approx 0.001$.

When a large number of time constants is required to describe adequately the course of the reaction it is probably most useful to adopt the mean first passage time as a measure of the reaction rate. This somewhat digressive topic is discussed next, but in Section V the emphasis is again on the ordinary case in which $\kappa^{-1} \gg \tau_1$, and for which the mean first passage time reduces simply to κ^{-1}.

B. Mean First Passage Time

Let $t_1, t_2, t_3, \ldots$ be the times which elapse before the molecules numbered 1, 2, 3, . . . react and are removed from the system. The mean first passage time $\bar{t}$ is defined as

$$\bar{t} = C(0)^{-1}(t_1 + t_2 + t_3 + \cdots)$$

where $C(0)$, according to Eq. (23), is the number of reactant molecules present at the beginning of the reaction. This definition is equivalent[4,7] to

$$\bar{t} = C(0)^{-1} \int_0^\infty C(t)dt \tag{26}$$

Define

$$\tau(x) = C(0)^{-1} \int_0^\infty c(x,t)dt$$

so that from Eqs. (23) and (26),

$$\bar{t} = \int_{\mathcal{R}} \tau(x)dx \tag{27}$$

while from Eq. (21),

$$-C(0)^{-1}c(x,0) = \int_{\mathcal{R}} k(y,x)\tau(y)dy - Z\tau(x) \tag{28}$$

Thus, according to Eqs. (27) and (28) the mean first passage time can be obtained by solving the integral equation for $\tau(x)$ and then integrating the result over all reactant states.

In the quantum formalism, with a finite number of reactant states, Eq. (28) can be solved by Cramer's rule, thereby leading to a determinantal formula for $\bar{t}$. Such a formula was given by Kim,[4] though Z did not appear in it because the completeness condition of Eq. (9) was not used.

Another method[19] of obtaining $\bar{t}$ is to solve Eq. (28) by means of a Liouville–Neumann expansion, which leads to the result

$$\bar{t} = Z^{-1}[1 + C(0)^{-1} \sum_{n=1}^{\infty} Z^{-n} \int_{\mathcal{R}} \int_{\mathcal{R}} k_n(y,x)c(y,0)dydx]$$

where $k_n(y,x)$ is the iterated kernel

$$k_n(y,x) = \int_{\mathcal{R}} \cdots \int_{\mathcal{R}} k(y,w_{n-1})k(w_{n-1},w_{n-2}) \cdots$$
$$k(w_2,w_1)k(w_1,x)dw_1 \cdots dw_{n-1}$$

with $k_1(y,x) = k(y,x)$. In this expression for $\bar{t}$ the successive terms may be interpreted[19] as the contributions to $\bar{t}$ made by those molecules which fail to react after one collision, by those which fail to react after two collisions, ...

Still another formula for $\bar{t}$ follows from Eqs. (16), (17), (20), (23), (25), and (26). It is to be recalled that in discussing a rate equation, the integrations in Eq. (17) are over $\mathscr{R}$, and $(Z - \mu_0)$ is κ, not 0. Then

$$\bar{t} = \sum_{i=0}^{\infty} W_i \tau_i$$

where for uniformity κ^{-1} is called τ_0, and where

$$W_i = \frac{\int_{\mathscr{R}} f(x)^{\frac{1}{2}} \phi_i(x)dx \int_{\mathscr{R}} f(x)^{-\frac{1}{2}} \phi_i(x)c(x,0)dx}{\int_{\mathscr{R}} \phi_i^2(x)dx \int_{\mathscr{R}} c(x,0)dx}$$

Although it is true that

$$\sum_{i=0}^{\infty} W_i = 1$$

one should not look upon $\bar{t}$ as an average τ_i because the W_i are not necessarily all positive.

It was noted in Section III-B that when the chemical reaction amounts to only a small perturbation of the reference relaxation system, then $\phi_0(x)$ is only a slightly perturbed form of $f(x)^{\frac{1}{2}}$. Therefore, also, $f(x)^{\frac{1}{2}}$ is practically orthogonal to all the $\phi_i(x)$ with $i = 1, 2, \ldots$. Thus, $W_0 \sim 1$ and $W \sim 0$ $(i = 1, 2, \ldots)$ whenever $\tau_0 \gg \tau_i$ $(i = 1, 2, \ldots)$, so

$$\bar{t} \sim \tau_0 = \kappa^{-1}$$

In other words, when the reaction is slow, so that the characteristic reaction time κ^{-1} is well separated from the relaxation times, then the mean first passage time is practically the same as κ^{-1}. The same conclusion follows even more simply, under the same assumptions, from Eqs. (24)–(26).

These expressions for $\bar{t}$ show that in general it depends on the initial distribution $c(x,0)$, so that it is not a time constant in the usual sense, and it becomes one only in the limit in which it approaches κ^{-1}.

V. STEADY-STATE AND EQUILIBRIUM DISTRIBUTIONS

A. Existence and Nature of the Steady State

If the system were in equilibrium one would have $c(x,t)/c(y,t) = f(x)/f(y)$, independently of the time t, that is, the distribution would be *steady* in the sense that the ratio of the populations in any two states would be independent of the time, and the steady distribution would in this case be the Boltzmann distribution. Of course, if the system were in equilibrium, then not only the ratio $c(x,t)/c(y,t)$, but also $c(x,t)$ and $c(y,t)$ separately, would be independent of the time, but the expression *steady state* will be used to describe the more general situation in which the population of any state may change with time, but the ratio of populations of any two states does not.

With the time evolution of the reaction system being given by Eq. (16), it is seen that after the elapse of a time long compared to the relaxation time,

$$c(x,t)/c(y,t) = f(x)^{\frac{1}{2}}\phi_0(x)/f(y)^{\frac{1}{2}}\phi_0(y) \tag{29}$$

so that the reaction not only proceeds from this point on in such a way as to be characterized by a single time constant $\kappa^{-1} = (Z - \mu_0)^{-1}$, but also, during this subsequent period, the reactants are in a steady state. The steady-state distribution is $f(x)^{\frac{1}{2}}\phi_0(x)$, and this approximates the Boltzmann distribution $f(x)$ only insofar as $\phi_0(x)$ approximates $f(x)^{\frac{1}{2}}$, that is, only insofar as the reaction proceeds slowly enough to be a small perturbation of the reference relaxation system. The reaction is said to have perturbed the Boltzmann distribution of reactant molecules. The initial period of relaxation is the time in which the steady-state distribution is established, and this distribution which the relaxation processes establish is independent of the initial distribution $c(x,0)$.

To understand physically the way in which the steady-state and Boltzmann distributions differ, imagine that at first reactants and products are in equilibrium, so that the reactant distribution coincides with the Boltzmann distribution. Then remove, instantaneously, all product molecules, and continue to do so the instant new ones are formed by reaction. Then all reactant states will be depleted, but the more reactive states will lose a greater fraction of their molecules than will the less reactive states, until a new steady condition is achieved. The steady-state distribution which is established is then, in comparison with the equilibrium distribution, poorer in the more reactive molecules and richer in the less reactive molecules. *The steady-state distribution is inherently less reactive than the equilibrium distribution,* and reaction from the former is necessarily slower than from the latter. At equilibrium, the inverse reaction replenishes the reactant states, and, by detailed balance, the more reactive of the reactant states are replenished preferentially. But when product molecules are removed instantaneously there is no preferential replenishment to balance the preferential depletion of the more reactive states.

B. Steady-State and Equilibrium Rate Constants

The probability per unit time that a molecule A in reactant state x will make a transition to *some* product state is

$$Q(x) = \int_{\mathscr{P}} k(x,y)dy = Z - \int_{\mathscr{R}} k(x,y)dy \qquad (x \text{ in } \mathscr{R}) \tag{30}$$

the second equality following from the completeness condition of Eq. (8). This is the reaction probability per unit time from reactant state x, and it is a measure of the inherent reactivity of molecules in that state. Necessarily,

$$0 \leqslant Q(x) \leqslant Z$$

whatever the state x.

The fraction of the reactant molecules which react per unit time, at the time t, may be expressed as

$$C(t)^{-1} \int_{\mathscr{R}} Q(x)c(x,t)dx$$

where $C(t)$, in accord with the definition in Eq. (23), is the total number of reactant molecules present at time t. It is precisely this fraction which is ordinarily identified as the rate constant for the reaction in Eq. (1), quite independently of whether the inverse reaction is or is not simultaneously occurring. Since $C(t)^{-1}c(x,t)dx$ is the fraction of all reactant molecules which, at time t, are in reactant states x in dx, the quantity $C(t)^{-1}c(x,t)$ is the (normalized) reactant distribution at time t. If averages over this reactant distribution are symbolized by $\langle\ \rangle$, then the definition of the rate constant just given can be written

$$\text{Rate constant} = \langle Q \rangle \tag{31}$$

that is, the rate constant is the mean value of the reaction probability per unit time. When the reactant distribution is time-dependent, as $C(t)^{-1}c(x,t)$ generally is, the resulting rate constant is time-dependent, and it therefore is not a rate constant in any ordinary sense. But when the reactant distribution is steady, i.e., when for any two reactant states x and y the ratio $c(x,t)/c(y,t)$ is independent of the time, then the mean of the reaction probability per unit time is constant and the system should be characterized by an ordinary phenomenological rate constant which is calculable from Eq. (31).

Two important cases in which the reactant distribution is steady occur when (*1*) products are instantaneously removed, and the relaxation time has elapsed, and (*2*) the system is in equilibrium.

In the first of these cases the steady reactant distribution was seen in Section V-A to be $f(x)^{\frac{1}{2}}\phi_0(x)$. When this is normalized and when the rate constant κ is then calculated from Eq. (31),

$$\kappa = \int_{\mathscr{R}} Q(x) f(x)^{\frac{1}{2}}\phi_0(x)\,dx \Big/ \int_{\mathscr{R}} f(x)^{\frac{1}{2}}\phi_0(x)\,dx$$

But from the definition of $Q(x)$ in Eq. (30), from the definition of the symmetrized transition kernel $S(x,y)$ in Eq. (14), and from the fact that $\phi_0(x)$ is an eigenfunction of $S(x,y)$ in $\mathscr{R}$ with eigenvalue μ_0, it follows that the rate constant κ obtained in this way is

$$\kappa = Z - \mu_0$$

in exact agreement with the earlier identification in Eq. (25).

In the second case the steady distribution of reactant molecules is the equilibrium distribution, and here the rate constant calculated from Eq. (31) and from the definition of $Q(x)$ in Eq. (30) is

$$\begin{aligned}\kappa_{\text{eq}} &= \int_{\mathscr{P}}\int_{\mathscr{R}} f(x)k(x,y)\,dx\,dy \Big/ \int_{\mathscr{R}} f(x)\,dx \\ &= Z - \int_{\mathscr{R}}\int_{\mathscr{R}} f(x)k(x,y)\,dx\,dy \Big/ \int_{\mathscr{R}} f(x)\,dx \end{aligned} \tag{32}$$

This is often[3,22] expressed in terms of the reaction cross-section from reactant state x, which is related to $\sigma(x,y;E)$ in the same way that the reaction probability per unit time $Q(x)$ is related to $k(x,y)$; then the alternative expression for κ_{eq} follows from Eqs. (5) and (32).

If the reaction is an isomerization rather than a dissociation, the present formalism applies to the inverse reaction as well as to the forward reaction. If κ_{eq}^f is then the equilibrium rate constant for the reaction $\mathscr{R} \rightarrow \mathscr{P}$ and κ_{eq}^b for the reaction $\mathscr{P} \rightarrow \mathscr{R}$, it follows from Eq. (32), and from the condition of detailed balance in Eq. (6), that

$$\kappa_{\text{eq}}^f/\kappa_{\text{eq}}^b = \int_{\mathscr{P}} f(x)dx \Big/ \int_{\mathscr{R}} f(x)dx$$

But the right-hand side is the ratio of partition functions, that is, the equilibrium constant K, so

$$\kappa_{\text{eq}}^f/\kappa_{\text{eq}}^b = K$$

It is important to note that *only the equilibrium rate constants are related in this way; the steady-state rate constants are not.*[9]

The fact that the steady-state rate constant κ differs from the equilibrium rate constant κ_{eq} illustrates an interesting notion due to Ross and Mazur,[13] viz., that a rate constant is affinity-dependent. From this point of view, since κ characterizes a system in which reaction products are instantaneously removed, it is the rate constant at infinite affinity, and since κ_{eq} characterizes a system in which products and reactants are in equilibrium, it is the rate constant at zero affinity. Suppose a reaction system is prepared with all the A molecules initially in reactant states but with product molecules allowed to accumulate. Presumably in the initial relaxation period there will be established a distribution of reactants identical to that found when products are instantaneously removed, and the reaction will then proceed with a rate constant κ; but as products gradually accumulate the reactant distribution will gradually approach the equilibrium distribution, and the rate constant will gradually (and, as seems likely, monotonically) approach κ_{eq}. Thus, whether the reaction proceeds the whole way from initiation to completion with a single rate constant or with a varying rate constant depends entirely on whether there is a measurable difference between κ and κ_{eq}.

The difference $(\kappa_{\text{eq}} - \kappa)$ is discussed further in Section V-C, but two more points may be noted here.

1. Whether the distribution of reactants is close enough to an equilibrium distribution to allow the rate constant to be approximated by κ_{eq} does not depend on having product molecules present, for the reverse reaction of product molecules to form reactants is only one of several possible mechanisms by which an equilibrium distribution of reactants may be maintained. As was seen in Section V-A, the reaction may be so slow that even when products are instantaneously removed from the system the steady-state distribution $f(x)^{\frac{1}{2}}\phi_0(x)$ may be close to the equilibrium distribution $f(x)$. Alternatively, the equilibrium distribution among reactant states may be maintained by an external agency in some special experimental arrangement.

2. Whether κ is close to κ_{eq} or not, the latter is an upper limit to the former:

$$\kappa_{\text{eq}} > \kappa \tag{33}$$

This follows from the discussion of Section V-A, where it was seen that reaction from the steady-state distribution is necessarily slower than reaction from the equilibrium distribution. The same result may be derived more formally, but less physically, from a well-known variational principle. Since $\kappa = (Z - \mu_0)$,

$$\kappa = Z - \int_{\mathscr{R}}\int_{\mathscr{R}} \phi_0(x)\phi_0(y)S(x,y)dx\,dy \Big/ \int_{\mathscr{R}} \phi_0^2(x)dx$$

where $\phi_0(x)$ is the eigenfunction of $S(x,y)$ that belongs to the eigenvalue μ_0. Furthermore, μ_0 is the *largest* eigenvalue. But if in the integrals appearing in the last equation one replaces $\phi_0(x)$ by $f(x)^{\frac{1}{2}}$ then, according to Eqs. (14) and (32), the right-hand side becomes κ_{eq}. The inequality (33) then follows from the extremal principle.

C. Difference Between the Steady-State and Equilibrium Rate Constants

A quantity $Q(x)$ was introduced in Section V-B as the reaction probability per unit time from reactant state x, and it was seen that

$$\kappa = \langle Q \rangle_{\text{s.s.}} \qquad \kappa_{\text{eq}} = \langle Q \rangle_{\text{eq}}$$

where $\langle\ \rangle_{\mathrm{s.s.}}$ and $\langle\ \rangle_{\mathrm{eq}}$ imply averages over the steady-state distribution $f(x)^{\frac{1}{2}}\phi_0(x)$ and over the Boltzmann distribution $f(x)$, respectively. It was, furthermore, inferred earlier that these two distributions would differ only very slightly if the reaction were slow. Since $Q(x)$ is itself a measure of reactivity, or of reaction rate, it might be anticipated that the difference $(\kappa_{\mathrm{eq}} - \kappa)$ would then be expressible as a series of terms of increasing order in Q. This is indeed the case, and it has been shown[21] that κ and κ_{eq}, each of which is of first order in Q, differ by a quantity which is of the second order in Q:

$$\kappa = \kappa_{\mathrm{eq}} - \bar{\tau}(\langle Q^2\rangle_{\mathrm{eq}} - \langle Q\rangle_{\mathrm{eq}}^2) + \cdots \tag{34}$$

where $\langle Q\rangle_{\mathrm{eq}}$ can be replaced by κ_{eq} at will, and where $\bar{\tau}$ is a certain mean relaxation time, that is, a certain average of the quantities $\tau_1, \tau_2, \ldots$ given by Eq. (20). Note that $\kappa < \kappa_{\mathrm{eq}}$, in agreement with the inequality (33). The result quoted in Eq. (34) may be derived from conventional second-order perturbation theory, treating the true symmetrized transition kernel $S(x,y)$ as a perturbed form of the $S(x,y)$ appropriate to the reference relaxation model (see Sections III and IV-A), for which $Q(x) \equiv 0$. Whether the relaxation times that enter $\bar{\tau}$ are those for the true reaction system or those for the reference relaxation system is a matter of no consequence, because the difference between these two sets of relaxation times vanishes with vanishing reaction rate.

In the reference relaxation system, where reaction does not occur, the relaxation processes establish a Boltzmann distribution, but when reaction competes with relaxation a compromise distribution, the steady state, is established instead. If, however, the relaxation processes were infinitely fast, that is, if the mean relaxation time $\bar{\tau}$ were zero, then in spite of the reaction the relaxation processes would be capable of maintaining a full equilibrium distribution, and there would then be no difference between κ and κ_{eq}. Thus, $(\kappa_{\mathrm{eq}} - \kappa)$ should vanish when $\bar{\tau}$ vanishes, in agreement with Eq. (34). Furthermore, it was seen earlier that the steady-state distribution differs from the equilibrium distribution because the reaction preferentially depletes the most reactive states. Then if all reactant states were of equal reactivity, so that $Q(x)$ were constant and $\langle Q^2\rangle_{\mathrm{eq}} = \langle Q\rangle_{\mathrm{eq}}^2$, there would again be no difference between the steady-state and Boltzmann distributions, and therefore again no difference between κ and κ_{eq}, and this, too, is in agreement with Eq. (34).

The quantities $\langle Q\rangle_{\text{eq}} = \kappa_{\text{eq}}$ and $\bar{\tau}$ are very familiar and have magnitudes which are well known from innumerable experiments, but the magnitude of the less familiar quantity $\langle Q^2\rangle_{\text{eq}}$ will also have to be inferred before Eq. (34) can be applied to estimate the difference $(\kappa_{\text{eq}} - \kappa)$. The most convenient measure of the order of magnitude of these kinetic variables is $\exp(-\varepsilon_0/kT)$, under the usual circumstances where this quantity is very much less than unity. Thus, in orders of magnitude,

$$\begin{aligned} \langle Q\rangle_{\text{eq}} &= Z \exp(-\varepsilon_0/kT) \\ \bar{\tau}\langle Q^2\rangle_{\text{eq}} &= Z \exp(-n\varepsilon_0/kT) \\ \bar{\tau}\langle Q\rangle_{\text{eq}}^2 &= Z \exp(-2\varepsilon_0/kT) \end{aligned}$$

and the problem is to estimate n.

Since a mean square is never less than a square mean, and since $\exp(-\varepsilon_0/kT) \ll 1$, it follows that $n \leqslant 2$. Since $Q(x)$ cannot exceed Z for any reactant state x, it follows that $\bar{\tau}\langle Q^2\rangle_{\text{eq}}$ cannot exceed $\langle Q\rangle_{\text{eq}}$ in order of magnitude, so $n \geqslant 1$. Thus,

$$1 \leqslant n \leqslant 2$$

It is impossible to narrow the range of n any further, and yet include all possibilities, since a model is known[21] which has the property that as a single physical parameter varies over the entire range to which it has access, n varies over the *entire* interval $1 < n \leqslant 2$. Therefore, any value of n in the interval 1 to 2 is a theoretical possibility, although in practice the range of n may be considerably more restricted.

If n were as large as 2 then the difference between κ and κ_{eq} would be of the order of magnitude of $\exp(-2\varepsilon_0/kT)$ and so, under ordinary circumstances, would be quite negligible. At the other extreme, if n were as small as 1 then the difference between κ and κ_{eq} would be of the order of magnitude of either one separately, and the distinction between them would then be of extreme importance. It will appear below that in real chemical systems n surely has neither of these extreme values, so that $1 < n < 2$; but that it can be expected to lie much closer to

1 than to 2, so that $\kappa/\kappa_{\mathrm{eq}}$ will be significantly less than unity when the temperature is high enough for kT to be comparable to a *small fraction*, $n - 1$, of ε_0. Whenever there is a measurable discrepancy between κ and κ_{eq} it can be expected to increase with temperature, because the higher the temperature the greater the reaction rate, and the faster the reaction the greater the difference between the steady-state and equilibrium distributions.

The parameter n is a measure of the extent to which the reaction probability per unit time $Q(x)$ actually varies from one reactant state x to another. If all reactant states, however low their energy, were of roughly equal reactivity (surely the exact opposite of the truth!) then $Q(x)$ would be approximately constant, $\langle Q^2\rangle_{\mathrm{eq}}$ and $\langle Q\rangle^2_{\mathrm{eq}}$ would be approximately equal, and therefore n would be close to 2. At the opposite extreme, if $Q(x)$ were identically zero unless the energy of state x were *at least* within a few kT of ε_0, and if $Q(x)$ were then essentially Z, one would have, in order of magnitude, $\langle Q^2\rangle_{\mathrm{eq}} = Z^2 \exp(-\varepsilon_0/kT)$, so that $n = 1$. Such a $Q(x)$ is often considered a reasonable idealization of a true $Q(x)$, and while a true $Q(x)$ would probably not vary quite so sharply as this, it is overwhelmingly likely to be much closer to this extreme than to the extreme of near constancy. Thus, n is surely in the interval $1 < n < 2$, and it seems highly likely that it is much closer to 1 than to 2. The implication of this is that the deviation of κ from κ_{eq} should be a real and measurable phenomenon. Indeed, it has been suggested[12,21] that this phenomenon may already have been observed.

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